ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

AGET ATRP OF STYRENE USING PMDETA AS BOTH LIGAND AND REDUCING AGENT

M.Sc. THESIS

Merve BAYRAKTAR

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

PMDETA'NIN LİGAND VE İNDİRGEN OLARAK STİRENİN AGET ATRP METHODUNDA KULLANIMI

YÜKSEK LİSANS TEZİ

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Merve Bayraktar, a **M.Sc.** student of **Institute of Science and Technology/ Graduate School of Istanbul Technical University** student ID **515121015**, successfully defended the **thesis** entitled **"AGET ATRP OF STYRENE USING PMDETA AS BOTH LIGAND AND REDUCING AGENT"**, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To Bayraktar Family,

FOREWORD

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Merve BAYRAKTAR
Chemist

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ABBREVIATIONS

AGET	**:** Activators Generated by Electron Transfer
ARGET	**:** Activators Re-Generated by Electron Transfer
ARTP	**:** Atom Transfer Radical Polymerization
CRP	**:** Controlled Radical Polymerization
CEF	**:** Chain End Functionality
DCF	**:** Dead Chains Fraction
DMF	**:** Dimethyl formamide
DMSO	**:** Dimethyl sulfoxide
DP	**:** Degrees of Polymerization
DPT	**:** Targeted Degree of Polymerization
EBrPr	**:** Ethyl-2-bromopropionate
FRP	**:** Free Radical Polymerization
IP	**:** Induction Period
k_{act}	**:** Activation Rate Constant
k_{deact}	**:** Deactivation Rate Constant
k_p	**:** Propagation Rate Constant
k_p^{app}	**:** Apparent Rate Constant
k_t	**:** Termination Rate Constant
K_{ATRP}	**:** Rate of ATRP Equilibrium
K_{BH}	**:** Rate of Alkyl Halide Bond Homolysis
K_{EA}	**:** Rate of Electron Affinity
K_{ET}	**:** Rate of Electron Transfer
K_X	**:** Rate of Halidophilicity
M_t^n **–X/Ligand**	**:** Metal Catalyst Complex at Lower Oxidation State
M_t^{n+1} **–X/Ligand**	**:** Metal Catalyst Complex at Higher Oxidation State
M_n	**:** Number Average Molecular Weight
M_w	**:** Weight Average Molecular Weight
MMA	**:** Methyl(meth acrylate)
MeOH	**:** Methanol
PMDETA	**:** N,N,N',N",N"-Pentamethyldiethylenetriamine
PRE	**:** Persistent Radical Effect
$R^{\cdot}$	**:** Radical Species
RAFT	**:** Reversible Addition Fragmentation Chain Transfer Polymerization
R-X	**:** Halogen Capped State
SFRP/NMP	**:** Stable Free Radical Polymerization/Nitroxide Mediated Polymerization
SR&NI	**:** Simultaneous Reverse and Normal Iinitiation
St	**:** Styrene
X	**:** Halogen

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AGET ATRP OF STYRENE USING PMDETA AS BOTH LIGAND AND REDUCING AGENT

SUMMARY

Controlled radical polymerization (CRP) has become one of the most powerful techniques for polymer synthesis during the past decade because of the ability to employ newly developed procedures to generate well-designed (co)polymers. Atom transfer radical polymerization (ATRP) is one of the most impressive controlled/living radical polymerization techniques to obtain effective control over molecular weights, narrow molecular weight distributions, functionalities, architectures. On the other hand, normal ATRP has some notable drawbacks such as using air or other oxidant sensitive catalyst and necessity of additional purification of the obtained polymer from a catalyst. In order to overcome these drawbacks of normal ATRP, activator generated by electron transfer atom transfer radical polymerization (AGET ATRP) which obtains effective system to reduce catalyst usage was developed. In a typical AGET ATRP system, a transition metal salt in its higher oxidation state, such as Cu (II) complex, is used as catalyst instead of lower oxidation state metal salt for normal ATRP system. AGET ATRP shows the advantages of easy preparation, storage, and handling of ATRP catalysts. Thus, the AGET ATRP was more suitable than normal ATRP, although in AGET ATRP external reducing agents such as ascorbic acid, D-glucose, and phenol. Apart from these external reducing agents, new nitrogen-based ligands that can serve as both ligand and reducing agent for AGET ATRP were developed.

By virtue of AGET ATRP process, because of the presence of higher oxidation state catalyst, reducing agents play a dramatic key role in controlling the dynamic equilibrium between a dormant species and propagating radicals via a reversible deactivation procedure and acting the polymerization to perform a successful AGET ATRP process.

In this study, AGET ATRP of styrene (St) in toluene and dimethylformamide (DMF) to compare low and high polar solvents (provide heterogeneous and homogeneous conditions, respectively) using air-stable $CuBr_2$ and in the specified ratios $CuBr_2$-CuBr mixtures as the catalyst and N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA) as both ligand and reducing agent were performed. AGET ATRP of styrene could been controlled well under heterogeneous and homogeneous conditions.

PMDETA'NIN LİGAND VE İNDİRGEN OLARAK STİRENİN AGET ATRP METHODUNDA KULLANIMI

ÖZET

Sentetik polimer kimyasında üstün özelliklere sahip yeni polimerik malzemelerin tasarımı ileri teknoloji malzemelerin hazırlanabilmesi açısından oldukça büyük öneme sahiptir. Bir polimerde istenen bütün özelliklerin homopolimer üzerinde sağlanması mümkün olmadığından, istenilen özellikleri içeren uygun homopolimer ile faz ayrımı olmadan blok ve graft kopolimerler sentezlenebilir. Yaşayan polimerizasyon teknikleri ile kontol edilebilen moleküller ağırlık ve moleküler ağırlık dağılımına sahip kompleks polimerler sentezi gerçekleştirilebilir. Kontrollü radikal polimerizasyonu aktif olmayan türlerle büyüyen türler arasındaki dinamik dengenin tersinir deaktivasyon işlemi sayesinde kontrol edilmesiyle sağlanır Kontrolü radikal polimerizasyon üzerine birçok çalışmalar yapılmış ve Tersinir Eklenme-Parçalanma Zincir Transferi (RAFT: Reversible Addition-Fragmentation Chain Transfer), Nitroksit Aracılıklı Polimerizasyon (NMP: Nitroxide Mediated Polymerization), Atom Transfer Radikal Polimerizasyonu (ATRP) gibi bazı methodlar önerilmiştir.

Atom Transfer Radikal Polimerizasyonu (ATRP) monomer, transfer edilebilir (psödo) halojene sahip başlatıcı ve her hangi bir ligand ile uyumlu geçiş metal komplesinin oluşturduğu bir katalizörü içeren çoklu bileşenli bir sistem olup en ilgi çekici olan kontrollü yaşayan polimerizasyon methodlarından biridir. ATRP'de büyüyen radikaller geçiş metal kompleksi ile halojenli türlerin değişimi ile sağlanan dinamik denge sayesinde tersinir olarak aktive ve deaktive edilebilir. ATRP ile başarılı bir polimerleşme gerçekleştirmek için çözücü ve sıcaklık da dikkate alınması gereken parametrelerdendir. Atom Transfer Radikal Polimerizasyonu (ATRP) tahmini molekül ağırlığı, dar düşük molekül ağırlığı dağılımı, çok değişken zincir uç fonksiyonalitesi ve kontrol edilebilen molekül yapısı üzerine etkin kontrol sağlayan en etkili kontrollü radikal polimerizasyonlarından biridir.

ATRP' de kullanılan özel Cu(I), Co, Rh, Fe, …/Ligand sistemi sayesinde katalizlenen bu metotta monomerler büyüyen polimer zincirine eklenebilir. Bu denge organik halojen ile Cu(I) tuzları gibi geçiş metali arasındaki redoks reaksiyonu üzerinden karbon-halojen bağının tersinir homolitik bölünmesini içerir.

ATRP'den önce ortaya çıkan kontrollü polimerleşme yöntemlerinde her türlü monomer kullanılamamasına karşın, ATRP mekanizması ile geniş bir monomer seçkisi polimerleşme için kullanılabilir. Özellikle bakır kompleksli ATRP sistemleri, stiren, akrilat, metaktilat, akrilonitril, izopren, akrilamid gibi yaygın kullanılan monomerlerin kontrollü/yaşayan (ko)polimerizasyonu için başarılı şekilde uygulanabilmektedir.

Kontrollü ve düzenli büyüyen polimer zinciri ve düşük moleküler ağırlık dağılımı, ATRP mekanizması sırasında kullanılan metal bazlı katalizör sayesinde elde edilir.

Metal bazlı katalizör, aktif büyüyen polimer zinciri ile durağan polimer bileşiği arasında bir denge kurulmasını sağlar. Böylece yan reaksiyonların oluşmasını ve istenmeyen sonlanmayı engeller; dolayısıyla molekül ağırlığının kontrol edilmesine imkân verir. Katalizör büyüyen zincirle reaksiyona girmediği için hem homojen hem de heterojen sistemde benzer özellik gösterir.

ATRP mekanizması içinde kullanılan monomer ve istenen reaktiviteye göre birçok farklı ligand kullanılabilir. En çok kullanılanları ise PMe_6TREN (Tris-[2-dimetil aminoetil]amin) ve TPMA (tris[(2-piridil)metil]amin)'dir; çünkü bu ligandlar ile yüksek bağlanma ve ayrışma hızları ile yüksek reaksiyon hızı elde edilir. Başlatıcı olarak alkil bromid gibi organik halidler kullanılabilir. Katalizör seçimi ise kontrollü büyüme için çok önemlidir. Çünkü katalizör ATRP mekanizması içindeki tepkimelerin dengesini sağlayan en büyük etmendir. Uyumlu, ucuz olması ve verimliliği sebebiyle bakır içeren katalizörlerin kullanımı yaygındır.

Fakat normal ATRP'nin hava ve diğer oksidantlara karşı hassas katalizör kullanımı, yüksek miktarda katalizör kullanımı ve katalizörün polimerden uzaklaştırılması için ileri saflaştıma işlemi gerektirmesi gibi bazı dikkate değer dezavantajları vardır. ATRP'nin bu dezavantajlarının üstesinden gelebilmek için, katalizör kullanımını azaltmayı sağlayan Elektron Transferi ile Aktifleştirici Oluşturan Atom Transfer Radikal Polimerizasyonu (AGET ATRP) geliştirilmiştir. Geliştirilen bu yöntemde normal ATRP için kullanılan düşük oksidasyon basamağındaki geçiş metal tuzu yerine, Cu(II) gibi yüksek oksidasyon basamağındaki geçiş metal kompleksi kullanımı genel AGET ATRP sisteminin temelini oluşturmaktadır. AGET ATRP yönteminde yüksek oksidasyon basamağındaki geçiş metalinin polimerizasyona etkili olabilmesi için in-situ da indirgen prosesi ilk olarak değişik fenolik bileşiklerinin indirgen ajan kullanılmasıyla Hizal ve meslektaşları tarafından gerçekleştirilmiştir. Bu gösterimden sonra Matyjaszewski ve Jakubowski ($Sn(EH)_2$) nin AGET ATRP de etkili şekilde kullanılabildiği gösterdikten sonra Matyjaszewski bir başka çalışmada askorbik asitin de indirgen olarak kullanılabildiğini gösterilmiştir.

AGET ATRP, normal ATRP prosesini az miktardaki katalizörün çok daha fazla miktardaki indirgen ajanla kullanılmasıyla ilerlemesine izin verir. Az miktarda kullanılan katalizör sadece çevre dostu bir polimerizasyon sağlamakla kalmayıp ayrıca gelişmiş zincir ucu fonksiyonalitesine ve düşük moleküler ağırlığı dağılımına sahip uzun polimer zinciri oluşumunu etkileyebilecek polimer uç grubu ile katalizör arasında gerçekleşebilecek yan reaksiyonları da önemli ölçüde engelmektedir. Her ne kadar AGET ATRP' e daha yüksek oksidayon basamağında bulunan metali indirgemek için askorbik asit, D-glukoz ve fenol gibi indirgen ajanların eklenmesi gerekse de AGET ATRP kolay hazırlama, depolama, katalizörün elde edilmesi açısından normal ATRP'ye göre daha uygun bir yöntemdir. Ekstra eklenen bu indirgen ajanların dışında polimerizasyon sırasında kullanılan ATRP bileşenlerinden bazılarının doğasında indirgeme özelliği bulunan moleküller geliştirildi. Bu bağlamda yapısında tersiyer amin grubu barındıran 2-(dimetiamino)etil metakrilat (DMAEMA) hem monomer hem de indirgen ajan görevini yerine getirerek ekstra indirgen ajan kullanımına gerek duyulmaksızın AGET ATRP yöntemiyle polimerleşme başarılı şekilde gerçekleştirilmiştir. Bunun yanısıra molekül yapısında fosfor ve amin gibi indirgeyici özellik sağlayan grupları barındıran ligandlar hem ligand hem de indirgen ajan görevini üstenen kullanılması yaygın olarak kullanılmaktadır.

AGET ATRP sistemininin doğasınca, AGET ATRP'de kullanılan katalizörün yüksek oksidasyon basamağında olmasından dolayı, indirgen ajanlar polimerizasyon sırasında aktif olmayan türlerle büyüyen türler arasındaki dinamik dengenin tersinir deaktivasyon işlemi sayesinde kontrol edilmesi ve polimerizasyonun ilerlemesi açısından, başarılı bir AGET ATRP gerçekleştirmek için oldukça önemli göreve sahiptir.

Bu çalışmada; oldukça yaygın kullanım alanına sahip stiren monomerinin, homojen ve heterojen ortamlardaki faklılıklarını göstermek amacıyla, toluen ve dimetilformamid (DMF) içerisindeki, havada kararlı halde bulunan $CuBr_2$ nin ve belirli oranlardaki $CuBr_2$-CuBr karışımlarının katalizör, N,N,N′,N″,N″-pentametildietilentriaminin (PMDETA) hem ligand hem de indirgen ajan görevlerini yerine getirdiği AGET ATRP yönetmiyle polimerleşmesi detaylı bir şekilde incelenmiştir.

1. INTRODUCTION

Controlled radical polymerization (CRP) has become one of the most powerful techniques for polymer synthesis during the past decade because of the ability to employ newly developed procedures to (co)polymerize a wide range of commercially available vinyl monomers to yield well-defined (co)polymers with desired architecture [1-2]. CRP can be achieved by maintaining a dynamic equilibrium between a dormant species and propagating radicals via a reversible deactivation procedure [3].

ATRP [4-6] is one of the most efficient CRP techniques allowing the synthesis of well-defined block copolymers with predictable molecular weight, narrow molecular weight distribution, wide range of functionalities, high degree of chain end-functionality and controllable macromolecular architecture [7].

However, normal ATRP has one notable limitation that is the catalyst used sensitive to air and other oxidant [8]. In order to overcome this drawback of normal ATRP, first study that Hizal and co-workers demonstrated generation and regeneration of Cu (I) species via electrontransfer in situ. The reduction reaction was obtained using phenoxide or p-methoxyphenol as a reducing agent of Cu (II). Then they showed that copper-catalyzed controlled/living radical polymerization of styrene was conducted using the silica gel-supported $CuCl_2$/PMDETA complex as catalyst [9].

After that Matyjaszewski's group has progress on the same ATRP technique, namely activator generated by electron transfer atom transfer radical polymerization (AGET ATRP) [10]. In a typical AGET ATRP system, a transition metal complex in its higher oxidation state metal salt, such as Cu (II), is used as catalyst complex instead of lower oxidation state metal salt for normal ATRP system. AGET ATRP shows the advantages of easy preparation, storage, and handling of ATRP catalysts. Thus, the AGET ATRP was more suitable than normal ATRP; although in AGET ATRP was required additional reducing agent.

Matyjaszewski and Jakubowski used tin(II) 2-ethylhexanoate ($Sn(EH)_2$) as a reducing agent of various Cu(II) complexes in ATRP of different monomer/catalyst precursor systems such as n-butyl acrylate and methyl methacrylate with $CuBr_2$/PMDETA to demonstrate the generality of AGET ATRP. The reduced in situ active catalyst complexes achieved controlled polymerization with a range of monomers that resulted in synthesis of well-defined polymers with controlled degree of polymerization and molecular weight distribution [10].

Again, Matyjaszewski's group investigated AGET ATRP of oligo (ethylene glycol) monomethyl ether methacrylates (OEOMA) in water at ambient temperature using tris [(2-pyridyl)-methyl] amine (TPMA)/$CuBr_2$ complex as an oxidatively stable Cu (II) precursor. In this instance, ascorbic acid was used as a reducing agent to reduce the air-stable Cu (II) salt, resulting in generation of an active catalyst. And they demostrated that the relative and absolute concentrations of the Cu(II)/ligand complex and ascorbic acid are important for control over AGET ATRP in water (Table 1.1) [11].

Table 1.1 : Detailed experimental conditions and properties of final P(OEOMA300) prepared by AGET ATRP in water at 30 °C with a Cu(II)/TPMA complex.

Entry	[OEOMA300] : [PEO5000-Br] : [$CuBr_2$-TPMA] : [AscA]	Time (min)	Conv.	$M_{n,theo}$	$M_{n,GPC}$	PDI
1	300:1:1:0.3	40	0.87	87500	112000	1.59
2	300:1:1:0.08	60	0.51	50600	51300	1.15
3	300:1:0.5:0.008	40	0.80	75600	71800	1.29
4	300:1:0.5:0.04	50	0.48	45500	50600	1.21
5	300:1:0.25:0.04	52	0.54	51100	63000	1.32

A development an ARGET ATRP of 2-(dimethylamino)ethyl methacrylate (DMAEMA) in the presence of limited amounts of air was reported by Dong and Matyjaszewski. The polymerization was successfully carried out without the addition of external reducing agents because DMAEMA serves as an internal reducing agent due to its tertiary amine group [12]. This technique potentially can be applied to other ATRP component containing functional reducing moieties, such as amines or phenols.

Shen and co-workers reported ARGET ATRP using Cu(II)Br_2/N,N,N′,N′-tetra[(2 pyrydal)methyl]ethylenediamine (TPEN) complex with 10-to 100-fold excess of tertiary amine. The tertiary amine was used as the reducing agent and Cu(II)Br_2/TPEN was used as the catalyst and well-controlled AGET ATRPs were obtained with 1 mol-% of catalyst relative to initiator, to produce PMA, PSt, and PMMA with molecular weights close to theoretical values and with low polydispersities [13].

Cu(II)Br_2 species with excess aliphatic nitrogen-based ligands such bpy, TMEDA, PMDETA or HMTETA were successfully applied to well-controlled polymerization of MMA via ARGET ATRP by Kwak and Matyjaszewski. A guideline for selection of an efficient ligand/reducing agent to generate well-defined low-polydispersity polymer under either homogeneous or under heterogeneous conditions was provided [14].

Lai and co-workers reported ATRP of MMA in PEG using different initiating systems with varied [$CuBr_2$]/[TMEDA]. They represented (Table 1.2) that with an increase the ratio of [$CuBr_2$]/[TMEDA] from 1 to 4, the rate of the polymerization was accelerated and all polymers was shown relatively low PDI values [15].

Table 1.2 : AGET ATRP of MMA in PEG(600) with different amounts TMEDA. [MMA]:[EBiB]:[$CuBr_2$]=100:1:1 at 80 ^oC.

Entry	[$CuBr_2$]:[TMEDA]	Time (min)	Conv. (%)	$M_{n,theo}$	$M_{n,GPC}$	PDI
1	1:1	45	44.0	4400	8900	1.15
2	1:2	45	52.6	5300	9500	1.15
3	1:3	45	69.2	6900	11100	1.17
4	1:4	45	89.5	9000	12500	1.18

Chen and his collegues firstly used HMTETA (Table 1.3) and PMDETA as both ligand and reducing agent in AGET ATRP for AN with $CuBr_2$ as catalyst in DMF. Then they showed that polymerization with HMTETA was controlled better than with PMDETA as both ligand and reducing agent. As more HMTETA was added, the monomer conversion increased with an increase of the molecular weight distribution. The rate of AGET ATRP of AN with DMF as solvent was faster than with acetonitrile, cyclohexanone, toluene, and xylene as solvents (Table 1.4) [16].

Table 1.3 : Effect of HMTETA content on AGET ATRP of AN with [AN]=5.5 M and [AN]:[EBiB]:[$CuBr_2$]=200:1:1 at 65 ^oC.

Entry	[$CuBr_2$]:[HMETETA]	Time (h)	Conv. (%)	$M_{n,theo}$	$M_{n,GPC}$	PDI
1	1:1	8	65.4	6932	22510	1.16
2	1:2	8	70.3	7452	26570	1.18
3	1:3	8	79.8	8459	29450	1.19
4	1:4	8	84.7	8978	32040	1.27
5	1:5	8	88.9	9423	37860	1.31

Table 1.4 : Kinetic data for AGET ATRP of AN with [AN]=5.5 M, t=8 h and [AN]:[EBiB]:[$CuBr_2$]:[HMTETA]=200:1:1:3 in different solvent at 65 ^oC.

Entry	Solvent	Conv. (%)	M_n	PDI	k_p^{app} x10^5 (s^{-1})
1	DMF	79.8	29450	1.19	5.6
2	Acetonitrile	69.9	27620	1.31	4.2
3	Cyclohexanone	49.7	30120	1.42	2.4
4	Toluene	40.2	33870	1.58	1.8
5	Xylene	34.8	40130	1.66	1.5

2-(8-heptadecenyl)-4,5-dihydro-1H-imidazole-1-ethylamine (OLC) was first used as both ligand and reducing agent in ARGET ATRP of MMA with $CuBr_2$ as catalyst by Li and Lu. Since aliphatic nitrogen-based ligand served as both ligand and reducing agents to constantly regenerate ATRP activator, Cu(I) species from the Cu(II) species, they showed that as more OLC was added, the monomer conversion increased with an increase in the molecular weight distribution (Table 1.5) [17].

Table 1.5 : Kinetic data for ARGET ATRP of MMA [MMA]:[EBP]=200:1 for 8 h at 70 ^oC in anisole.

Entry	Catalyst	[Cu]/[ligand]	Conv. %	M_n	PDI	k_p^{app}x10^5 (s^{-1})
1	$CuBr_2$/bpy	1/2	86.68	17517	1.32	7.08
2	$CuBr_2$/OLC	1/1	57.47	11675	1.12	7.19
3	$CuBr_2$/OLC	1/2	63.46	12873	1.12	7.50
4	$CuBr_2$/OLC	1/3	70.26	14233	1.15	7.89
5	$CuBr_2$/OLC	1/4	78.22	15825	1.16	8.36
6	$CuBr_2$/OLC	1/10	87.65	17711	1.28	7.06

According to Kwak and Matyjaszewski, reporting the AGET ATRP process of styrenes and acrylates using nitrogen-based ligand reducing agent is an attractive study [14]. However, some side reactions such as transfer to acrylates and quaternization of amino groups by benzyl halides may become important [18-19].

The fountainhead of this study was that seeing the gap for ARGET ATRP were performed for most of monomers except styrene with linear amine ligand, therefore, AGET ATRP process of styrene using PMDETA as both ligand and reducing agent was detaily investigated.

2. THEORETICAL PART

2.1 Controlled/Living Radical Polymerizations

Free radical polymerization (FRP) is one of the most common and practical techniques for producing commodity polymers. FRP possesses great tolerance to material and operational impurities, along with high compatibility with a wide range of vinyl monomers making it a very robust and cost effective process that accounts for a significant portion of polymer production. Mechanistically, FRP with a thermal initiator can be broken down into three basic steps – initiator decomposition and initiation, propagation, and termination by combination or disproportionation as shown in Figure 2.1.

Initiator dissociation	$I \xrightarrow{k_d} 2R\cdot$
Initiation	$R\cdot + M \xrightarrow{k_i} P_1\cdot$
Propagation	$P_n\cdot + M \xrightarrow{k_p} P_{n+1}\cdot$
Termination by combination	$P_n\cdot + P_m\cdot \xrightarrow{k_{tc}} D_{n+m}$
Termination by disproportionation	$P_n\cdot + P_m\cdot \xrightarrow{k_{td}} D_n + D_m$

Figure 2.1 : FRP mechanism.

Due to the high reactivity of transient radical species, polymer chain lifetimes are short with unavoidable termination and transfer reactions that yield a broad molecular weight distribution with statistical polymer architecture. This makes it difficult to generate more complex and defined structures, which are required for advanced applications [20].

Living polymerizations such as anionic, cationic, coordination, ring opening polymerizations are almost free from side reactions such as termination and chain transfer reactions, and thus, can generate polymers with well defined architectures, controlled molecular weights and living end groups [21]. In addition, living polymerizations provide synthesis of polymers with low polydispersities. However,

monomers, polymerization conditions may be limited for the type of the living polymerization technique chosen. In some cases, functional groups on the monomers may result in side reactions, and thus, for some processes control over the polymerization can be difficult.

The main limitations of radical polymerization are the lack of control over the molar mass, the molar mass distribution, the end-functionalities and the macromolecular architecture. Mainly for that reason, the recent emergence of many so-called 'living' or controlled radical polymerization (CRP) processes has opened a new area in this old polymerization method that had witnessed relatively small progress in the previous years[2].

To overcome the limitations, CRP has been developed and there is a sharp increase in the number of the publications on the controlled radical processes from 1990s up to now. In CRP, synthesized polymers have narrow molecular weight distributions ($1.1<M_w/M_n<1.5$). The polymers obtained have living end groups. Different polymer architectures (linear, star, comb and branched) as well as polymer compositions (random, block, graft and gradient copolymers) can be achieved [7].

In the last 20 years, several methods of CRP have been introduced that allow for much greater control over polymer microstructure. The most studied methods of CRP are stable free radical polymerization/nitroxide mediated polymerization (SFRP/NMP) [22], reversible addition fragmentation chain transfer polymerization (RAFT) [23-24], and atom transfer radical polymerization (ATRP) [4, 25]. The central principle between all forms of CRP is to suppress bimolecular termination by maintaining a low radical concentration throughout the polymerization. This is accomplished through an equilibrium between dormant polymer chains which are capped by a mediating species, and active polymer chains which are free to undergo propagation and other FRP mechanisms. In order to successfully suppress termination, the equilibrium must favour the formation of dormant chains, and the formation of a dormant chain should be fast.

2.2 Atom Transfer Radical Polymerization (ATRP)

The pioneering work on ATRP was conducted independently by two groups in 1995. Kato et al.demonstrated the polymerization of methyl methacrylate (MMA) using a

ruthenium based complex [25], while at the same time Wang and Matyjaszewski showed the polymerization of styrene using a copper based mediator [4]. Since then, an immense amount of literature has been published on ATRP in bulk and solution, mostly using copper bound to a nitrogen based ligand as the mediating species due to its low cost and versatility compared to other transition metals [26-27].

In ATRP, growing radicals can be reversibly activated or deactivated via a dynamic equilibrium with a transition metal complex (Mt^n-X/Ligand) with an exchange of halide species (X) between the chain end and metal complex, as shown in Figure 2.2. As the rate coefficient for deactivation (k_{deact}) is much higher than the activation rate coefficient (k_{act}), the majority of chains exist in a dormant (halogen capped) state (R-X), thereby suppressing bimolecular radical termination and enabling control over polymer microstructure. In addition, unavoidable termination between radicals will lead to a build-up of deactivating species. This shifts the equilibrium towards the dormant state and further lowers the active radical concentration to suppress termination. This is also known as the persistent radical effect (PRE) [28].

In addition, k_{deact} is of a similar order of magnitude as that for k_t; as deactivator concentration is much higher than radical concentration, deactivation becomes the dominant chain ending reaction.

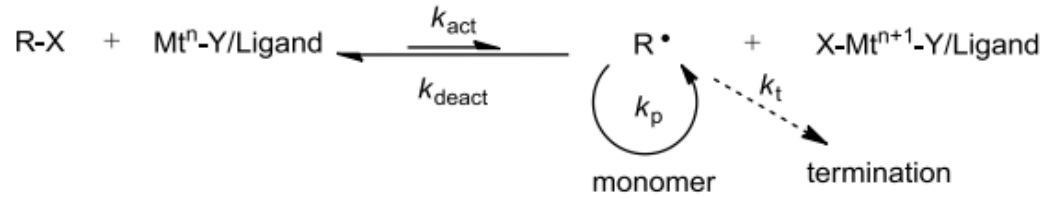


Figure 2.2 : General mechanism for ATRP.

Traditionally, the transition metal complex which governs the ATRP equilibrium is used in stoichiometric or slightly sub-stoichiometric ratio to the initiating alkyl halide species. The ratio of monomer to initiator provides the target molecular weight (M_w), and for the desired M_w in most applications this results in a high level of residual metal in the final polymer. The catalyst residue can be toxic and adds undesired colour to the polymer. Therefore, the catalyst residue must be reduced to a low level for most applications. The usual method of removing the

catalyst is that polymerization solution is passed though a column containing aluminum oxide. Another method is that polymers are purified by precipitation from acidified methanol solution instead of simply passing through aluminum oxide columns. The third method is the liquid– liquid extraction. The catalyst can be extracted from the organic phase to the water phase. Then the purified polymers can collected after evaporating solvent. This additional level of post-process purification can add significantly to production costs, and is a considerable hurdle towards commercial scale applications of ATRP [6, 29-30].

2.2.1 Components of ATRP

ATRP consists of the monomer, an initiator with a transferable (pseudo)halogen, and a catalyst (composed of a transition metal species with any suitable ligand), so Atrp is a multicomponent system.Sometimes an additive is used and to generate a successful ATRP solvent and temperature must be taken into consideration [26].

2.2.1.1 Monomers

A diverse range of monomers have been polymerized by way of ATRP Typical monomers include styrenes, (meth) acrylates, (meth)acrylamides, and acrylonitrile, which contain substituents that can stabilize the propagating radicals [31]. Although under the same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species because of their own intrinsic radical propagation rate. Thus, for a specific monomer, the concentration of propagating radicals and the rate of radical deactivation need to be adjusted to maintain polymerization control [32].

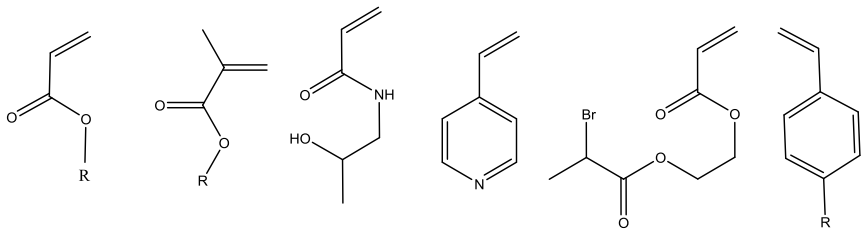
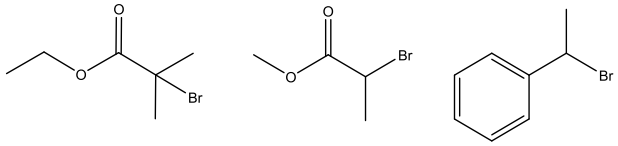


Figure 2.3 : Some of the monomers used in ATRP.

2.2.1.2 Initiator

An initiator is used to determine the number of growing polymer chain. In ATRP, R-X are typically used as the initiator and the rate of the polymerization is first order

with respect to the concentration of R-X [33]. The alkyl halides used as initiators can contain one or more halogen atoms. Depending on the exact initiator structure and the number of halogen atoms, the architecture of the prepared polymers can be varied from linear (using alkyl halides with a single halogen atom), to star-like or brush-like (multiple halogen atoms in the initiator) [18]. To obtain well-defined polymers with narrow molecular weight distributions, the halide groups, X, must rapidly and selectively migrate between the growing chain and the transition-metal complex [26-27].



EBiB MBrP PEBr

Figure 2.4 : Some of the most used initiator in ATRP.

2.2.1.3 Catalyts

The catalyst is the most important component of ATRP because it determines the equilibrium constant between the active and dormant species. This equilibrium determines the polymerization rate and an equilibrium constant too small may inhibit or slow the polymerization while an equilibrium constant too large leads to a high distribution of chain lengths [27]. There are several prerequisites for an efficient transition metal catalyst. First, the metal center must have at least two readily accessible oxidation states separated by one electron. Second, the metal center should have reasonable affinity toward a halogen. Third, the coordination sphere around the metal should be expandable upon oxidation to selectively accommodate a (pseudo)-halogen. Fourth, the ligand should complex the metal relatively strongly [26]. To differentiate ATRP from the conventional redox-initiated polymerization and induce a controlled process, the oxidized transition metal should rapidly deactivate the propagating polymer chains to form the dormant species [21]. As the catalyst, a variety of transition metal such as Cu, Fe, Ni, Ru have been used to compose complexes with various ligands have been studied in ATRP.

2.2.1.4 Ligands

The main roles of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential and halogenophilicity of the metal

center forming a complex with an appropriate reactivity and dynamics for the atom transfer.

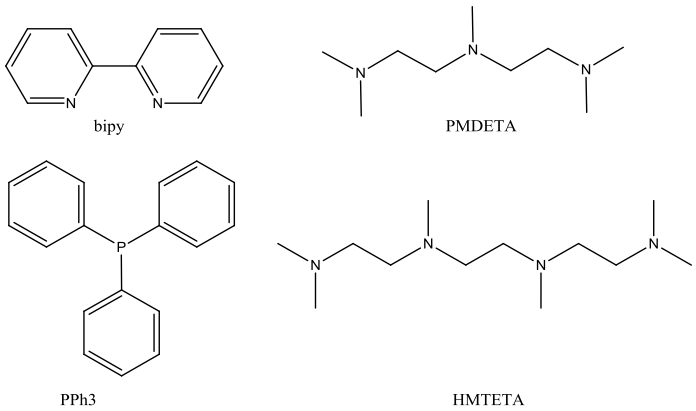


Figure 2.5 : Some of the most used ligands in ATRP.

2.2.1.5 Solvents

ATRP can be performed in all polymerization techniques: bulk, solution, emulsion, suspension. For different monomers, several solvents such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide have been used. Several factors affect the solvent choice. Chain transfer to solvent should be minimal. In addition, interactions between solvent and the catalytic system should be considered. Catalyst poisoning by the solvent and solvent-assisted side reactions should be minimized [34-35].

2.2.1.6 Temperature and reaction time

The rate of polymerization in ATRP increases with increasing temperature due to the increase of both the radical propagation rate constant and the atom transfer equilibrium constant. Because of the higher activation energy for the radical propagation than for the radical termination, higher k_p/k_t ratios and better control ("livingness") may be observed at higher temperatures. However, chain transfer and other side reactions become more pronounced at elevated temperatures. The optimal temperature depends mostly on the monomer, the catalyst, and the targeted molecular weight. Therefore, for successful ATRP, optimum temperature should be found depending on the monomer, catalyst and the other components of ATRP [26].

At high monomer conversions, the rate of propagation slows down considerably; however, the rate of any side reaction does not change significantly, as most of them are monomer concentration independent. Prolonged reaction times leading to nearly

complete monomer conversion may not increase the polydispersity of the final polymer but will induce loss of end groups [36].

2.2.2 ATRP Equlibrium

The dynamics of the ATRP equilibrium are very important to the polymerization rate and control imposed over the final macromolecular structure. As briefly discussed, the deactivation of growing chains must be fast in order to suppress unwanted radical termination. In addition, fast activation is required in order to maintain a reasonable rate of polymerization as well as to ensure that all chains are initiated at the same time. This ensures that all polymer chains grow at the same rate and undergo similar numbers of activation/deactivation cycle, statistically leading to a narrow final molecular weight distribution. As copper complexes are most often used in ATRP, the rate of polymerization for an ATRP system assuming negligible bimolecular termination can be approximated as [26]:

$$R_p = k_p[M][P^\bullet] = k_p[M]k_{act}/k_{deact}[R\text{-}X]_o\,([Cu^I])/([Cu^{II}]) \qquad \textbf{2-1}$$

where: k_p is the monomer propagation rate coefficient; [M], [$P^\bullet$], $[R\text{-}X]_o$ are monomer, propagating chain, and alkyl halide initiator concentrations respectively; k_{act} and k_{deact} are the rate constants of activation and deactivation which combine to form the ATRP equilibrium constant; and $[Cu^I]$ and $[Cu^{II}X]$ are the concentrations of the activator and deactivator species. Of the variables in Equation 2-1, the rate constants of activation (k_{act}) and deactivation (k_{deact}) exhibit the largest variance with polymerization conditions and are the key to successfully controlling the final molecular structure using ATRP.

The ATRP equilibrium can be theoretically broken down into 4 separate reversible reactions as shown in Figure 2.6. It is important to note that while analysis of the ATRP equilibrium as dissected into these four elementary steps can generate useful trends, the physical relevance to how the reaction proceeds is less meaningful. The four reversible reactions are: oxidation of the metal complex (electron transfer, K_{ET}), alkyl halide bond homolysis (K_{BH}), reduction of a halogen to a halide ion (electron affinity, K_{EA}), and association of the halide ion to metal complex (halidophilicity, K_X) [37]. The product of these four elementary rate constants gives rise to the overall ATRP equilibrium (K_{ATRP}).

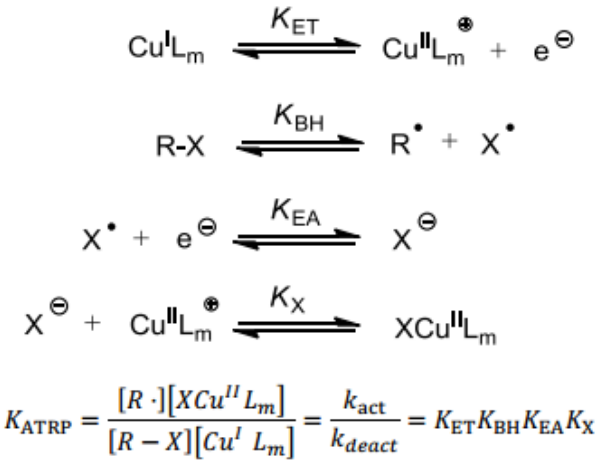


Figure 2.6 : Breakdown of the ATRP equilibrium.

2.2.2.1 Alkyl halide and copper halide bond strength

The effect of alkyl halide structure on the ATRP equilibrium can be generalized in order of radical stability (tertiary > secondary > primary). Tertiary radicals formed from methacrylic polymer chain ends or corresponding alkyl halides analogues have the greatest radical stability due to hyperconjugation with adjacent bonds and as such possess the highest k_{act}. Substituent effects on radical stability also apply, and electron rich α-substituents capable of stabilizing the radical will increase the activation rate constant [38-39].

The effect of halide on the ATRP equilibrium is more complex, and in general, K_{ATRP} of alkyl bromides are an order of magnitude higher than the corresponding chloride complex. This is the summation of several factors, the first being the strength of the carbon-halide bond. Carbon-chloride bonds are stronger than carbonbromide bonds, and as such, the higher bond dissociation energy for C-Cl bonds will lower K_{BH} and decrease K_{ATRP}. At the same time, chlorine has a greater electron affinity than bromine as it is more electronegative, and K_{EA} for chlorine will be higher. Finally, copper chloride bonds are stronger than copper bromide bonds, making the formation of the higher oxidation state complex more likely and thus increasing K_{ATRP} [37, 39-40].

2.2.2.2 Halidophilicity of metal center

In general, a metal center with higher affinity for halides forms more active ATRP complexes. A comparison between copper, ruthenium and osmium complexes used for ATRP found that ruthenium and osmium complexes with similar

ATRP activities were generally much less reducing when compared to copper complexes. The halide affinities (halidophilicity) of the ruthenium and osmium compounds were calculated to be 7-9 orders of magnitude stronger than typical copper ATRP complexes in order to compensate for the more positive reduction potentials [41].

2.2.2.3 Reduction potential of the mediating complex

The electron transfer equilibrium (K_{ET}) is mostly affected by ligand selection and has the largest influence on the ATRP equilibrium. There are a number of ligands available for copper mediated ATRP, and a selection of the ligands that have been studied are shown in Figure 2.7, with corresponding equilibrium constants spanning over 7 orders of magnitude [39, 42]. As k_{deact} is generally fast with small variability between mediating species, the shift in ATRP equilibrium comes from changes in the activation rate constant. It is difficult to relate directly ligand structure to the ATRP equilibrium, as small changes can have large effects on the activation kinetics likely due to steric constraints on copper/ligand complex geometry. This is best illustrated by comparing tris[2-(dimethylamino)ethyl]amine (Me_6TREN, highlighted in green), used to form one of the most active ATRP complexes, to tris[2-(diethylamino)ethyl]amine (Et_6TREN, highlighted in orange), a structurally similar ligand with similar electron donating substituents. Me_6TREN has a K_{ATRP} of 1.5×10^{-4}, while Et_6TREN has a K_{ATRP} of 9.4×10^{-10} under the same conditions, a difference of over 5 orders of magnitude.

Even with the apparent discrepancies, the general order of activity for copper complexes based on ligand structure increases with denticity [39]. A better way to identify the activity of a copper complex for ATRP is through its reduction potential. Complexes with lower (more negative) reduction potentials are more reducing and therefore more active than complexes with higherreduction potentials. This is illustrated in Figure 2.8, which shows a linear relationship between K_{ATRP} and redox potential for different copper complexes. Lower reduction potentials result in higher ATRP equilibrium constants and therefore higher polymerization rate [39].

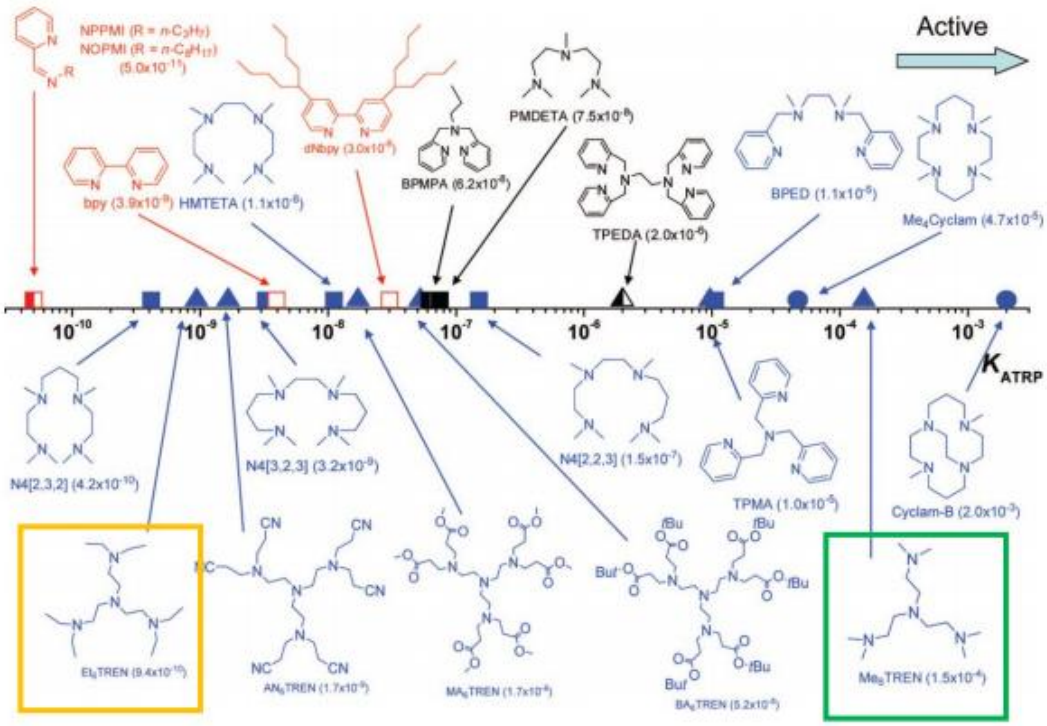


Figure 2.7 : Some of the most used ligands in ATRP ATRP equilibrium constants (K_{ATRP}) for various nitrogen based ligands as measured with CuBr in acetonitrile at 22 °C .

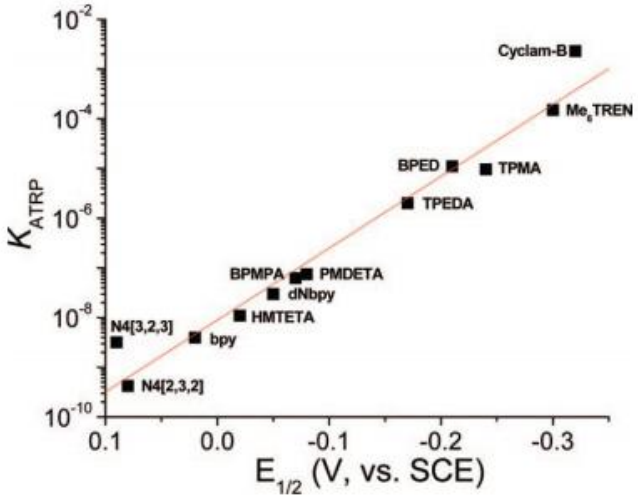


Figure 2.8 : Plot of K_{ATRP} vs. redox potential for copper complexes shown in Figure 2.7.

Another method of predicting the activity of a copper complex for ATRP is to compare the stability constants of the metal complex. A complex with a low reduction potential should be more stable in its oxidized state. In other words, the more stable the high oxidation state is compared to the low oxidation state, the lower the reduction potential between the two oxidation states and the more active

the copper complex becomes. Omitting the oxidation state for simplicity, the overall stability constant can be generally defined as [43]:

$$\beta_{k,\mathrm{L}} = \frac{[\mathrm{CuL}_k]}{[\mathrm{Cu}][\mathrm{L}]^k} \qquad \textbf{2-2}$$

Where: CuL_k is the concentration of the copper complex, Cu is the concentration of free copper species, and L is the concentration of free ligand. The redox potential of the copper complex can be approximated by the following relationship [37]:

$$\mathrm{E} \approx \mathrm{E}^\circ + \frac{\mathrm{RT}}{\mathrm{F}}\left(\ln\frac{[\mathrm{Cu}^{\mathrm{II}}]_{tot}}{[\mathrm{Cu}^{\mathrm{I}}]_{tot}} - \ln\frac{\beta^{\mathrm{II}}}{\beta^{\mathrm{I}}}\right) \qquad \textbf{2-3}$$

where: E° is the standard potential of the Cu^{II}/Cu^{I} couple, R is the universal gas constant, T is temperature, F is Faraday's constant, and β^j is the stability constant of the Cu^jL complex in the relevant oxidation state. As the stability constants are easily measured and readily available, it is possible to use the stability constant of each oxidation state to predict ATRP activity and the overall ATRP equilibrium.

The ATRP equilibrium and stability constants for some common ligands are given in Table 2.1. The stability constant of copper(I) and copper(II) complexes can be used to generate an estimate of the activity of the complex [37]. A high ratio of β^{II}/β^{I} indicates that the copper(II) oxidation state is more stable than the copper(I) state, and as such the complex should have a high activation rate constant. The ratio $\beta^{II}/(\beta^{I})^2$ can be used to estimate a complex's tendency to disproportionation and is discussed later during the overview of SET-LRP.

Table 2.1 : Comparison between stability constants and ATRP activity for ligand structures see Figure 2.1.

Copper comlex	β^{I}	β^{II}	$\log(\beta^{II}/\beta^{I})$	$\log(\beta^{II}/(\beta^{I})^2)$	K_{ATRP}
CuBr/bpy	8.9×10^{12}	4.5×10^{13}	0.70	-12.25	3.93×10^{-9}
CuBr/HMTETA	1×10^{11}	3.98×10^{12}	1.60	-9.40	8.38×10^{-9}
CuBr/PMDETA	$<1 \times 10^{8}$	1.45×10^{12}	4.16	-3.38	7.46×10^{-8}
CuBr/TPMA	7.94×10^{12}	3.89×10^{17}	4.69	-8.21	8.65×10^{-6}
CuBr/Me_6TREN	6.3×10^{8}	2.69×10^{15}	6.63	-2.17	1.54×10^{-4}

2.2.2.4 Solvent effects on ATRP equilibrium constant

Solvent choice can heavily impact polymerization kinetics in FRP through solvent interactions with monomer and transition state radical structures. In ATRP, solvent can affect the rate of polymerization and control over polymerization by impacting the propagation rate constant as in FRP, in addition to other properties of the transition metal complex. In general, it has been found that activation rate constants increase with solvent polarity. Using the four elementary reactions presented in Figure: 2.6, solvent effects can be broken down into its specific impact on each mechanism.

Without going into detailed calculations, solvent effects can be qualitatively analyzed in terms of stability. The electron affinity (K_{EA}) is affected by charge localization and ion solvation. Solvents which promote ion solvation and stabilize halide ions will give larger K_{ATRP}'s.

Halidophilicity (K_X) is influenced by similar factors, and the more poorly a halide ion is solvated, the more strongly it will bind to the metal center, and the more reducing the complex becomes. The solvent effect on electron transfer (K_{ET}) can likewise be characterized by its impact on complex stability at each oxidation state. As previously discussed, a copper complex that is more stable in its higher oxidation state will be more reducing and more active. Therefore, solvents, which preferentially stabilize the copper (II) oxidation state, will increase the ATRP equilibrium and the rate of polymerization. It should be noted that K_{ET} is still dominated by ligand choice, as the degrees of freedom afforded by the ligand will shape complex sensitivity to various solvents. This is due to possible reorganization of the coordination sphere upon oxidation and more rigid ligands like Me_4-cyclam make this process more difficult compared to a branched ligand with higher degree of freedom like Me_6TREN (see Figure 2.7 for ligand structures).

The Kamlet-Taft expression is a linear solvation energy relationship that has been used to describe and predict properties in solution such as solubility, free energy and enthalpy of equilibria, and redox potentials. The Kamlet-Taft equation is defined as [44]:

$$XYZ = XYZ_0 + \alpha \propto + b\beta + s\pi^* + h(\delta_H)^2 \qquad \textbf{2-4}$$

where: XYZ is the property of interest, XYZ_0, a, b, s, and h are solvent independent coefficients characteristic of the process; α is the hydrogen bond donor ability of the solvent, β is the hydrogen bond acceptor ability, π* is the dipolarity/polarizability parameter (ability of solvent to stabilize charge or dipole by its dielectric effect), and δ_H is the Hildebrand solubility parameter, which is a measure of the solvent-solvent interactions that are disrupted in creating a cavity for the solute. Kamlet-Taft relationships have been used by Coullerez et al. [45] and Brauecker et al.[46] to analyze and predict solvent effects on the ATRP equilibrium with good accuracy. ATRP equilibrium constants spanning over 7 orders of magnitude were predicted and compared to experimental results with strong agreement. Figure 2.9 shows a plot of predicted log(K_{ATRP}) compared to experimentally derived log(K_{ATRP}), and it can be seen that polar solvents like dimethyl sulfoxide (DMSO) possess substantially higher equilibrium constants than toluene or acetone [46].

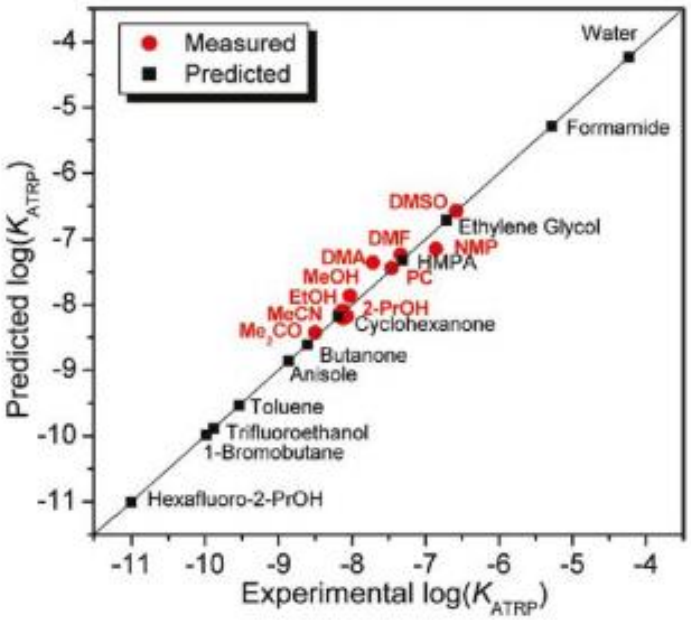


Figure 2.9 : log(K_{ATRP}) as predicted using the Kamlet Taft relationship vs. experimental log (K_{ATRP}).

2.3 Reverse ATRP

In ATRP, the polymeric chain growth is mediated by a transition-metal complex and the mechanism is outlined in Figure 2.2. A low radical concentration, which helps to minimize the termination reaction, can be maintained by a dynamic equilibrium

between the radical species ($R^{\cdot}$) and the dormant species (R–X) due to the redox reaction of the metal catalyst between the lower oxidation state (M_t^n–X/L) and higher oxidation state (X–M_t^{n+1}–X/L).

One limitation of "classical" ATRP was the relatively large amount of catalyst used relative to the monomers, so that the final products often contained a significant amount of residual metal. Various strategies were introduced either to remove the catalyst from the final products [6] or to carry out the reactions at lower catalyst concentration. However, the amount of catalyst cannot be decreased to desired low concentrations because of inevitable termination reactions. Additionally, polymerization systems, which are less oxidatively stable in large vessels and in aqueous media, are difficult to deoxygenate, which can lead to irreversible oxidation and loss of the ATRP activators.

Reverse ATRP is a convenient method to get over such oxidation problems. The ATRP initiator and lower oxidation state transition metal activator are generated in situ from conventional radical initiators and the higher oxidation state deactivators [47-48]. The initial polymerization components are thus less sensitive to oxygen in reverse ATRP and can therefore be easily prepared, stored, and shipped for commercial use. However, reverse ATRP has some limitations. The amount of catalyst cannot be independently reduced and should be comparable to the amount of radical initiator, because the added M_t^{n+1} complex provides the only source of the transferable atoms. Furthermore, a block copolymer cannot be synthesized using reverse ATRP.

These problems were partially solved by the development of the simultaneous reverse and normal initiation (SR & NI) process [48-49]. In this process, an ATRP initiator, that is, an alkyl halide or a halogen-terminated macroinitiator, is added to the reaction together with a conventional radical initiator. Both of them contribute to the ATRP equilibrium, so that the relative amount of catalyst can be dramatically decreased and the synthesis of block copolymers can be achieved. Indeed, SR & NI was successful for the preparation of homopolymers, linear block copolymers, star-block copolymers, and gradient copolymers with a significantly decreased concentration of catalyst in both bulk and miniemulsion processes. On the other hand, the SR & NI process had an intrinsic deficiency when it was used to synthesize block copolymers. This drawback [1] came from the use of a conventional radical

initiator to reduce the catalyst complex, which introduced new free radicals. These free radicals produced homopolymer chains consisting of the second monomer only, which competed with the growth of block copolymers from the macroinitiator. Therefore, the final product contained a small fraction of homopolymer in addition to the desired block copolymer. The limitation of SR & NI ATRP is evident in the inability of these techniques to produce clean block copolymers, because pure block copolymers are nearly impossible to obtain.

In order to overcome these drawbacks, more recently an improved ATRP technique, activators generated by electron transfer for ATRP (AGET ATRP) process, has been developed by Matyjaszewski's group [50]. The key of this process is the introduction of a reducing agent. A reducing agent, which is unable to initiate new chains (rather than organic radicals), is used in AGET ATRP to reduce the higher oxidation state transition metal complex to generate the active catalyst (the lower oxidation state transition metal complex) in situ (Figure 2.10). Therefore, no homopolymers are produced during block copolymerization by this technique, and it has been proven particularly useful in aqueous and miniemulsion systems [50].

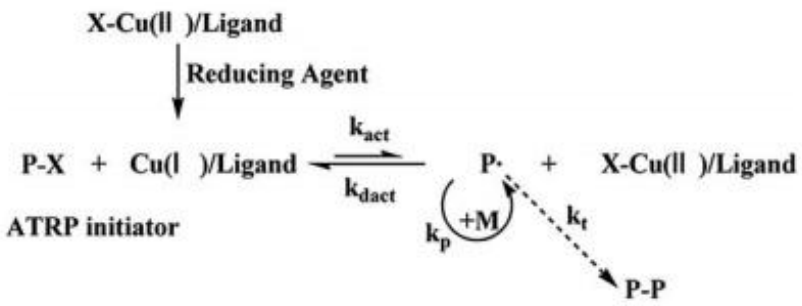


Figure 2.10 : Mechanism of AGET ATRP.

2.3.1 AGET ATRP

2.3.1.1 Basic components of AGET ATRP

As a multicomponent system, AGET ATRP is consist of a monomer, an initiator, a catalyst composed of a transition metal species with any suitable ligands, and reducing agents. Sometimes an additive is used. For a successful AGET ATRP, factors such as solvent and temperature must also be taken into consideration.

Typical monomers commonly used in AGET ATRP are acrylonitrile, (meth) acrylates, meth (acrylamides) and styrenes initiators include α-halonitriles, α-

haloesters, benzylic halides, and phenyl-ester halides. Due to regulation of the dynamic equilibrium between the dormant and propagating species, the complex of a metal and a ligand is the most important component of catalytic system [5]. For this aim, the copper complex with nitrogen-based ligands or iron complex with acid, nitrogen, or phosphorus based ligands are generally used. The reducing agents are used to react with the Cu(II) complexes to generate the Cu(I) ATRP activators. AGET principle was showed using tin(II) 2-ethylhexanoate ($Sn(EH)_2$) [10], ascorbic acid(AsAc) [50], or triethylamine[13] as the reducing agents. Apart from these, zero-valent metals [51], glucose [52], phenol [9], methylaluminoxane [53], and N_2H_4 [54] were also successfully used as efficient reducing agents in AGET ATRP. In some spesific cases where certain monomers or ligands can act as efficient reducing agents, there is no need to extra reducing agent in AGET ATRP process. As N,N-dimethylaminoethyl methacrylate (DMAEMA) [12] can be used as reducing monomer, copper (II) catalyzed nitrogen based N,N,N',N'-tetramethyl-ethylenediamine (TMEDA), 1,1,4,7,10,10-Hexamethyltriethylene tetramine (HMTETA), N,N,N′,N″,N″-Pentamethyldiethylenetriamine (PMDETA) [15-16, 55] and iron (III) catalyzed phosphorus ligands (2-[(diphenylphosphino)methyl]pyridine (DPPMP), 2-(diphenylphosphino)pyridine (DPPP) can act as both ligand and reducing agent [56].

2.3.1.2 Kinetics of AGET ATRP

Like ATRP, a successful AGET ATRP process should meet several requirements. Firstly, the initiator should be consumed in the early stages of polymerization and therefore generate propagating chains leading to polymers with degrees of polymerization (DP). Secondly, the molecular weight distribution (M_w/M_n) of the resultant polymers should be low since the number of monomer molecules added during one activation step should be small. Finally, the contribution of transfer and termination reactions should be negligible, enabling a high degree of end functionality.

Kinetics and controllability depend not only on the persistent radical but also on the activator (M_t^n/L). According to Equation 2-5, the polymerization rate increases with initiator concentration and actually depends on the ratio of activator to deactivator concentrations. The equation indicates that there is a constant concentration of active

species in the polymerization, and first order kinetics with respect to the monomer. On the other hand, molecular weight distribution (M_w/M_n) in AGET ATRP depends on the propagation rate constant (k_p), deactivation rate constant (k_{dact}), monomer conversion (p), and concentrations of initiator and deactivator ($X–M_t^{n+1}$), according to Equation 2-6. In addition, the molecular weight distribution (M_w/M_n) typically decreases with conversion and, in a well-controlled process, approaches a value that is close to 1.1.

$$R_p = k_p[M][P] = k_p K_{ATRP}[M][I]_o[M_t^n]/[X\text{-}M_t^{n+1}] \quad \textbf{2-5}$$

$$M_w/M_n = 1 + 1/DP_n + ([I]_o\, k_p/k_{dact}[X\text{-}M_t^{n+1}])(2/p\text{-}1) \quad \textbf{2-6}$$

$$-\Delta[M_t^n] = \Delta[P_t] = k_t[P]^2 t \quad \textbf{2-7}$$

$$DCF = 2\, DP_T k_t [\ln(1\text{-}p)]^2/[M]_o k_p^2 t \quad \textbf{2-8}$$

Well-defined functional polymers made by AGET ATRP require high chain end functionality (CEF) [57].According to Figure 2.10, negligible termination reactions occur due to the persistent radical effect. The amount of terminated chains depends on the concentration of propagating radicals, $P^{\cdot}$, and the rate constant of termination, k_t , according to Equation 2-7, Unavoidable radical termination reactions irreversibly consume activators, and reactions usually do not proceed to completion if the amount of Cu(I) initially added to the system is below 10 mol % of the initiator [58]. Some general rules, valid for all LRPs, that correlate the preserved CEF with polymerization rate were presented. In order to synthesize a polymer with a higher CEF at the same rate, a lower DPT (targeted degree of polymerization), lower conversion (*p*), higher initial monomer concentration, and bulk conditions should be used according to Equation 2-8 (DCF: dead chains fraction, Equation 2-9).

$$CEF = 1\text{-}DCF \quad \textbf{2-9}$$

For the synthesis of a polymer with a certain DP during the specific time frame, it is beneficial to target higher DPT and stop the reaction at lower conversion rather than the opposite way (lower DPTand higher conversion). The minimal polymerization

time for preserved CEF strongly depends on the monomer structure. Monomers with lower $k_t/(k_p)^2$ values allow a faster polymerization with the same CEF. Also, higher temperature and higher pressure are beneficial because they decrease $k_t/(k_p)^2$values.

2.3.2 ARGET ATRP

An ATRP catalyst that is sufficiently stable and active can be used at very low concentration. However, it is very important to mention that a catalyst in the lower oxidation state is constantly being converted to a complex in the higher oxidation state, as a result of unavoidable radical termination reactions. Therefore, the deactivator ($X–M_t^{n+1}$) will accumulate in the system as the reaction proceeds. The amount of the M_t^n complex lost due to termination is equal to the amount of terminated chains, as shown by Equation 2-6. Furthermore, accumulation of the deactivator ($X–M_t^{n+1}$) results in slowing down of the polymerization rate, which in turn prevents high monomer conversions. From Figure 2.11, it can be seen that AGET and ARGET ATRP share a great deal of similarities. Both techniques employ the more oxidatively stable copper(II) species as a starting material. This can simplify handling procedures as active copper complexes are readily oxidized in the presence of air from copper(I) to copper(II). The difference between the two methods lies in the amount of mediator and reducing agent added.

ARGET ATRP is similar to AGET ATRP as shown in Figure 2.11, with the exception that it utilizes much smaller concentrations of the activator, a much larger amount of ligands and consequently a large excess of the reducing agent relative to the deactivator. As a result, the deactivator that accumulates as a persistent radical is continuously reduced to the activator. An M_t^n complex is needed to homolytically cleave the alkyl halide bond (R–X). As indicated in Equation 2-4,the rate of monomer consumption in ATRP depends on the absolute ratio of the concentrations of activator ($X–M_t^n$) and deactivator ($X–M_t^{n+1}$). Therefore, the absolute amount of copper catalyst in ARGET ATRP can be decreased undernormal ATRP conditions without affecting the rate of polymerization.

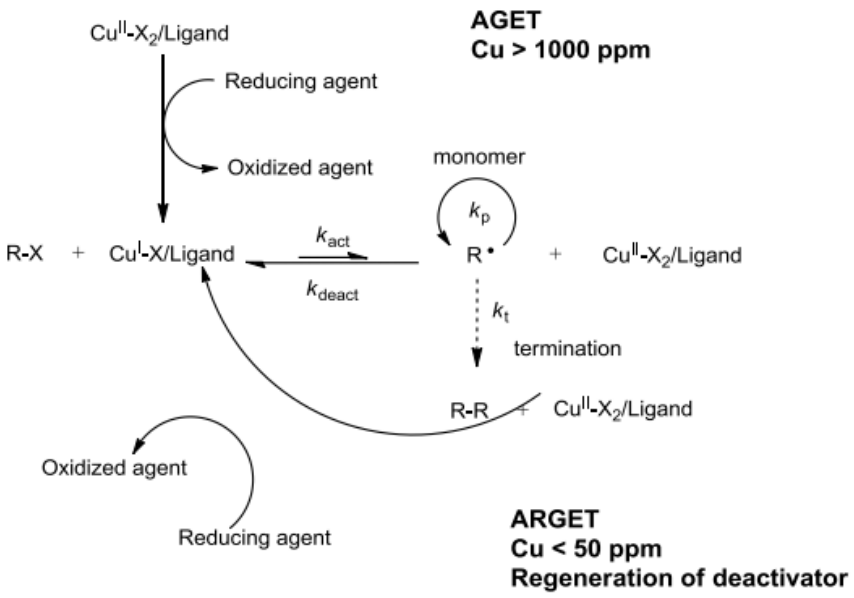


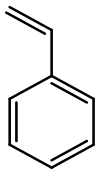
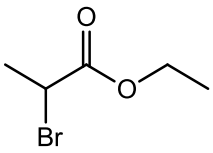
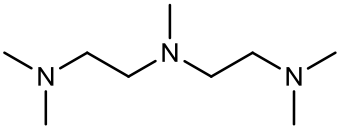
Figure 2.11 : Proposed mechanism for AGET and ARGET ATRP.

3. EXPERIMENTAL PART

3.1 Materials

N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMDETA, 99%), copper (I) bromide (CuBr, 99.99%) and copper (II) bromide ($CuBr_2$, 99.99%) were purchased from MERCK Milipore. Styrene (St, 99%) and ethyl-2-bromopropionate (EBrPr) were purchased from FLUKA Chemicals and ABCR GmbH & Co., respectively. N,N-dimethylformamide (DMF), toluene, methanol (MeOH) was purchased from CARLO ERBA Reagents. All reagents were used without further purification. Table 3.1 presents the chemical structures of all used chemicals

Table 3.1 : Used chemicals structures.

		
St	EBrPr	PMDETA

3.2 General procedure for AGET ATRP of styrene

A typical experimental procedure for polymerization was as follows: The calculated amount of $CuBr_2$ as catalyst was placed in a 48-mL Schlenk tube followed by degassing under vacuum and back-filling three times with N_2. Degassed solvent DMF (1 ml), a given amount of styrene as monomer, PMDETA as ligand, and EBrPr as initiator were added to a Schlenk flask respectively. The reactor was immersed in an oil bath at 110 °C under 500 rpm stirring rate. Samples were taken out from the flask periodically under nitrogen using a nitrogen-purged syringe to determine the monomer conversion by gravimetercally. The products PSt were obtained after

precipitation in MeOH (10 mL), filtration, washing, and drying in vacuo at 50 ^{o}C to constant weight.

3.3 Characterization

The conversion of the monomer was determined by gravimetrically.

The molecular weight (M_n) and PDI of PSt were measured by gel permeation chromatography (GPC). GPC was performed with a Waters 1515 solvent delivery system (Milford, MA) at a flow rate of 1.0 mL min^{-1} through a combination of Waters HT3, HT4, and HT5 styragel columns. PSt standards were used to calibrate the columns. The analysis was undertaken at 35 ^{o}C with purified high-performance-liquid-chromatography-grade THF as an eluent. A Waters 2414 differential refractometer was used as the detector.

4. RESULTS and DISCUSSION

The aim of this study is to show behavior of AGET ATRP system using PMDETA as both a nitrogen-based tri-dentate ligand and reducing agent for synthesis of well-defined PSt (Figure 4.1).

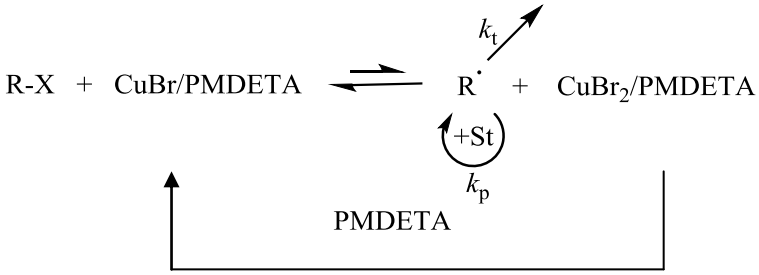


Figure 4.1 : Synthesis reaction of AGET ATRP.

4.1 AGET ATRP of Styrene without Reducing Agent

4.1.1 In polar solvent

Based on results presented below, AGET ATRP of St was performed using various ligand concentrations. Polymerizations were performed at 110 ^{o}C with a molar ratio of [St]:[EBrPr]:[$CuBr_2$]:[PMDETA] as 200:1:1:x in 10% (v/v) DMF under homogeneous conditions. In Figure 4.2 and Figure 4.3 were shown k_p^{app} and induction period (IP) versus different molar ratio of [PMDETA] using PMDETA as both ligand and reducing agent. It can be clearly seen from Figure 4.2, the polymerization was accelerated by increasing of PMDETA amount, the apparent rate constant reached up to certain value as 2.25×10^{-4} s^{-1}. This was because of non-equivalence of $CuBr_2$ and PMDETA in the solution. Increasing the amount of PMDETA resulted in the higher concentration of CuBr procuded by reduction of $CuBr_2$ salt, so increased concentrations of propagating radicals were generated until equivalence of metal/ligand complex was achieved. The amount of propagating radicals were designated the polymerization rate. As seen on Figure 4.3, the IP got shorter and reached limit value as 45 min with an increase in the content of PMDETA. This is fact that concentration of PMDETA/CuBr complex generated

from PMDETA/$CuBr_2$ was too low to produce enough propagating species during early stages of polymerizations. Therefore, the propagation of PSt chains was retarded. So, induction period was fixed by amount of PMDETA.

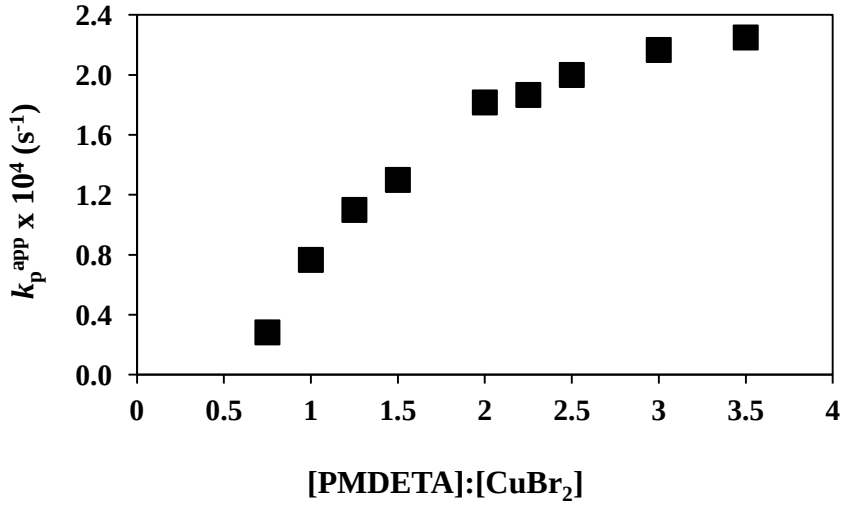


Figure 4.2 : Effect of PMDETA on k_p^{app} of AGET ATRP of St in 10% (v/v) DMF at 110 ^oC. [St]= 7.91 mol/L, [St]:[EBrPr]:[$CuBr_2$]= 200:1:1.

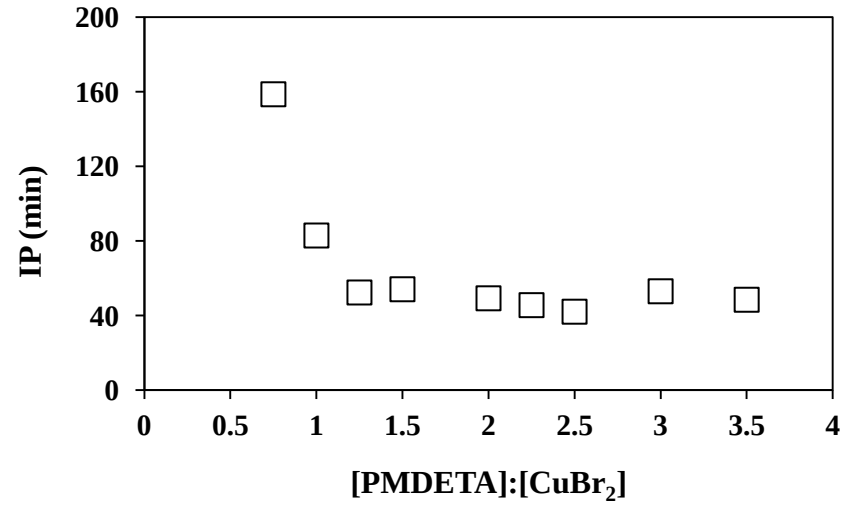


Figure 4.3 : Effect of PMDETA on IP of AGET ATRP of St in 10% (v/v) DMF at 110 ^oC. [St]= 7.91 mol/L, [St]:[EBrPr]:[$CuBr_2$]= 200:1:1.

To show effect of ligand on AGET ATRP, the polymerization was also carried out without PMDETA, besides with PMDETA, where the monomer conversion reached about 0.6% within 46 h. k_p^{app} and IP were calculated $2.5x10^{-7}$ s^{-1}, and 35.4 h from according to kinetic plots of, respectively. Therefore, it is possible to make inference that during AGET ATRP of St, free radical polymerization of St did not effect the monomer conversion relatively.

Not only $CuBr_2$ but also $CuBr_2$/CuBr mixtures were used as catalyst with molar ratio [St]:[EBrPr]:[$CuBr_2$+CuBr]:[PMDETA] as 200:1:1:1 in 10% (v/v) DMF at 110 ^oC. k_p^{app} and IP versus different molar ratio of [PMDETA] versus total catalyst amount were represented in Figure 4.4 and Figure 4.5. The apparent rate constant was linearly increased with the increasing of CuBr in the [$CuBr_2$+CuBr] from $7.67x10^{-5}$ to $1.15x10^{-4}$ (Figure 4.4). PMDETA is responsible for reduction and then formation of PMDETA/CuBr complex in $CuBr_2$ case, whereas it only behave formation of Ligand/catalyst complex in CuBr case. As seen on Figure 4.5, IP values were decreased with the increasing of CuBr amount in [CuBr+$CuBr_2$]. IP was reached to the expected "zero" value when the $CuBr_2$ is none in [CuBr+$CuBr_2$] where AGET ATRP turn to normal ATRP.

Additionally, Figure 4.6 is displayed the representative relationship between molecular weigt (M_n) and PDI versus monomer conversion belonging to AGET ATRP of St in the molar ratio of [St]:[EBrPr]:[$CuBr_2$]:[PMDETA]= 200:1:1:1. From Figure 4.6, M_n values of resultant polymers were increased linearly with monomer conversion and relatively low polydispersity (PDI≈1.1) are observed. These results demonstrated that any transfer reaction were not occured during polymerization; also as required resultant polymer chains had almost same monomer units. Therefore, it is possible to say that AGET ATRP of styrene with aliphatic nitrogen based ligands used as both reducing agents and ligands was generated as successfully and well controlled.

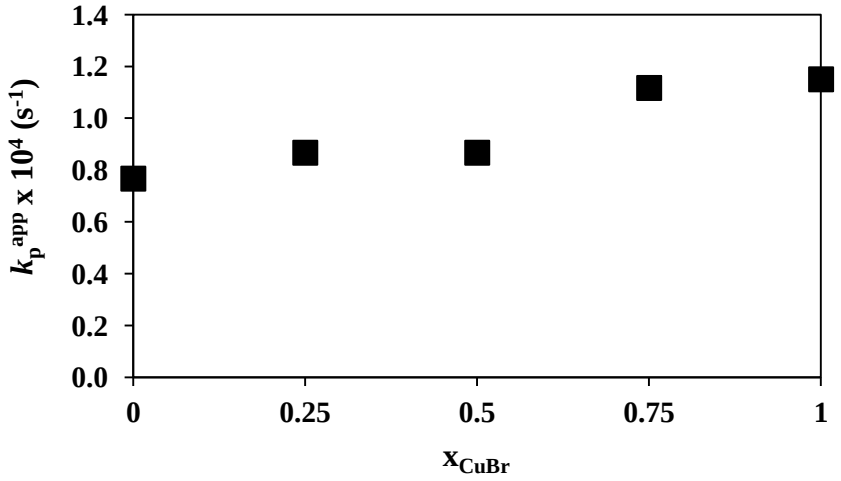


Figure 4.4 : Effect of CuBr fraction in the constant total catalyst amount ([$CuBr_2$+CuBr]) on k_p^{app} of AGET ATRP of St in 10% (v/v) DMF. [$CuBr_2$+CuBr]=$3.96x10^{-2}$mol/L,
[St]:[EBrPr]:[$CuBr_2$+CuBr]:[PMDETA]= 200:1:1:1 at 110 ˚C.

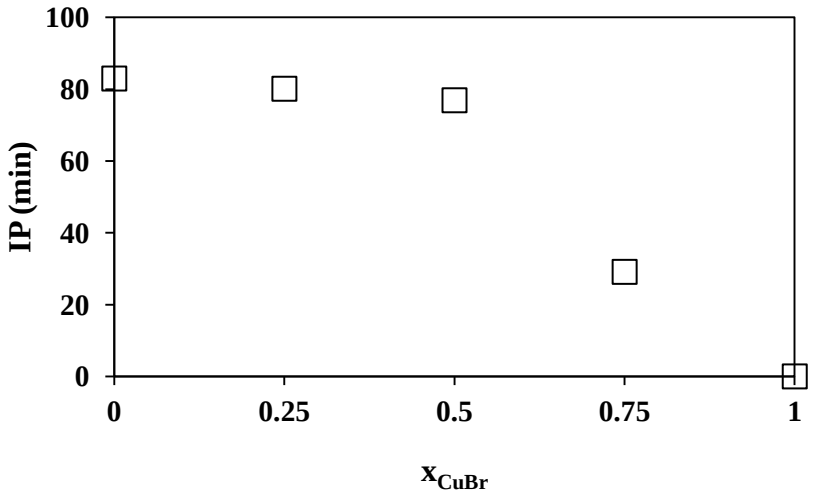


Figure 4.5 : Effect of CuBr fraction in the constant total catalyst amount ([$CuBr_2$+CuBr]) on IP of AGET ATRP of St in 10% (v/v) DMF. [$CuBr_2$+CuBr]=3.96x10^{-2}mol/L, [St]:[EBrPr]:[$CuBr_2$+CuBr]:[PMDETA]= 200:1:1:1 at 110 ˚C.

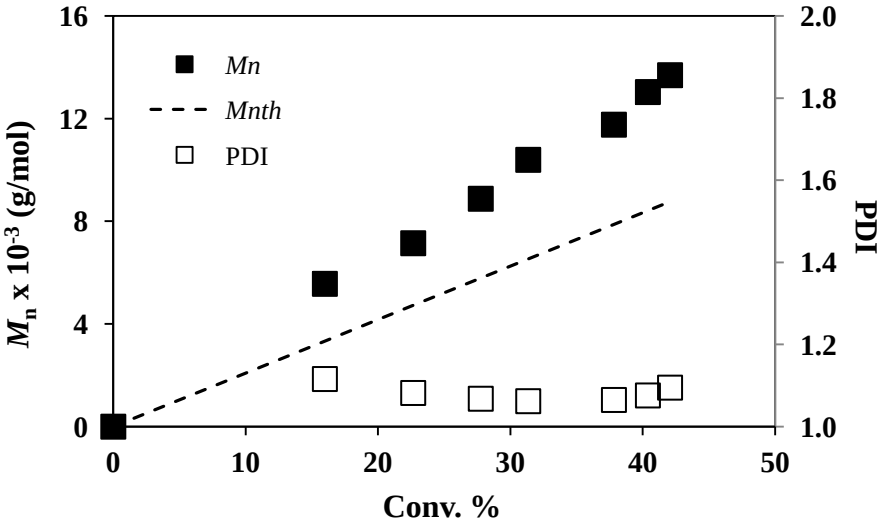


Figure 4.6 : Dependence of M_n and PDI on monomer conversion for AGET ATRP of St in 10% (v/v) DMF at 110 ^oC. [St]= 7.91 mol/L, [St]:[EBrPr]:[$CuBr_2$]:[PMDETA]= 200:1:1:1.

4.1.2 In nonpolar solvent

Adapted from results presented below, AGET ATRP of St was performed using a varity of ligand concentrations. Polymerizations were carried out with a molar ratio of [St]: [EBrPr]: [$CuBr_2$]: [PMDETA] as 200:1:1: x at 110 ^oC in 10% (v/v) toluene under heterogeneous conditions. In Figure 4.7 and Figure 4.8 were shown k_p^{app} and IP versus different molar ratio of [PMDETA] using PMDETA to reduce $CuBr_2$ to CuBr and form PMDETA/CuBr complex.

As seen on Figure 4.7, the polymerization was accelerated by increasing of PMDETA, the apparent rate constant reached up to plato value as $1.2x10^{-4}$ s^{-1} just as in homogenous conditions but lower than homogeneous system. However, under heteregenous conditions, i.e. in toluene, the amount of ligand for using the reduction of $CuBr_2$ was smaller than homogeneous conditions, i.e, in DMF. Figure 4.8, likewise in homogeneous conditions, with an increase in the content of PMDETA the induction period got shorter and reached certain value as 22 min. It seems that, the interaction between PMDETA and solute $CuBr_2$ in toluene was easier and induction period was shorter than DMF.

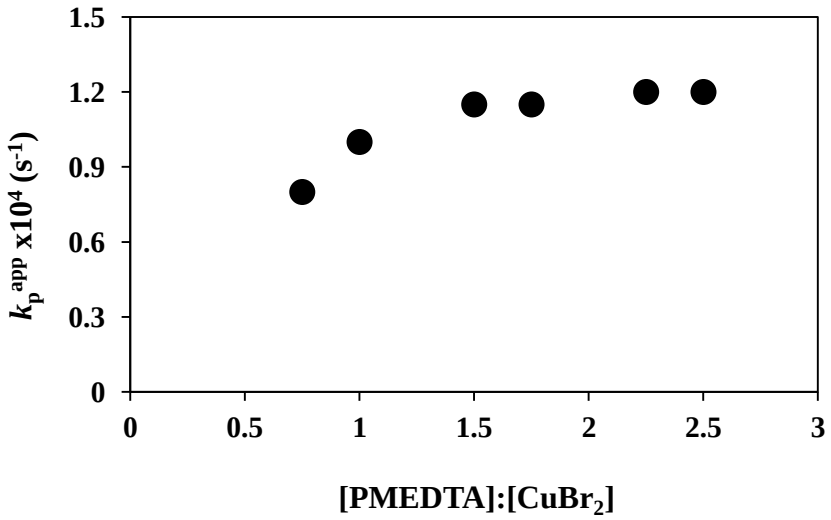


Figure 4.7 : Effect of PMDETA on k_p^{app} of AGET ATRP of St in 10% (v/v) toluene. [St]= 7.91 mol/L, [St]:[EBrPr]:[$CuBr_2$]= 200:1:1 at 110 ^oC.

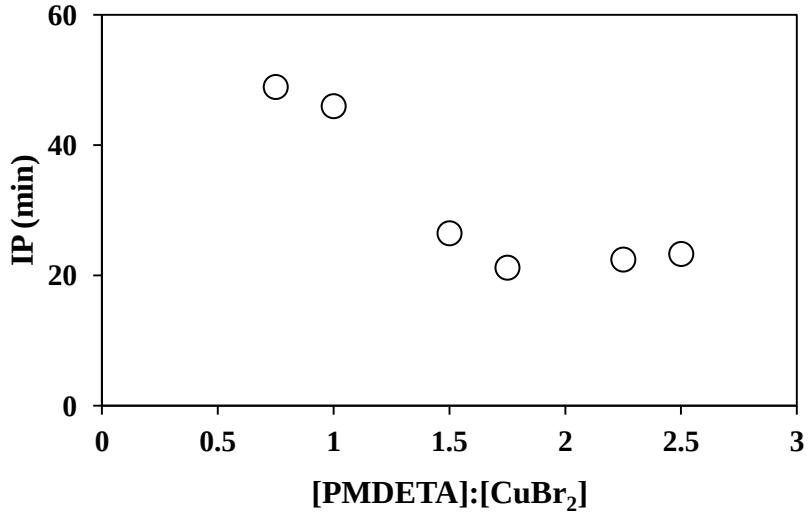


Figure 4.8 : Effect of PMDETA on IP of AGET ATRP of St in 10% (v/v) toluene. [St]= 7.91 mol/L, [St]:[EBrPr]:[$CuBr_2$]= 200:1:1 at 110 ^oC.

Moreover $CuBr_2$-CuBr mixture used as catalyst to generate polymerization in a ratio of [St]:[EBrPr]: [$CuBr_2$+CuBr]:[PMDETA] as 200:1:1:1 in toluene. k_p^{app} and IP versus different molar ratio of [PMDETA] were represented in Figure 4.9 and Figure 4.10. As seen on Figure 4.9, the apparent rate constant was rising from $1x10^{-4}$ to $1.75x10^{-4}$ with an increase in content of CuBr content in [$CuBr_2$+CuBr] and on Figure 4.10 induction period was decreased with the increasing of CuBr in [CuBr+$CuBr_2$] same as in DMF and reached to "0" when $CuBr_2$ in [CuBr+$CuBr_2$] is zero.

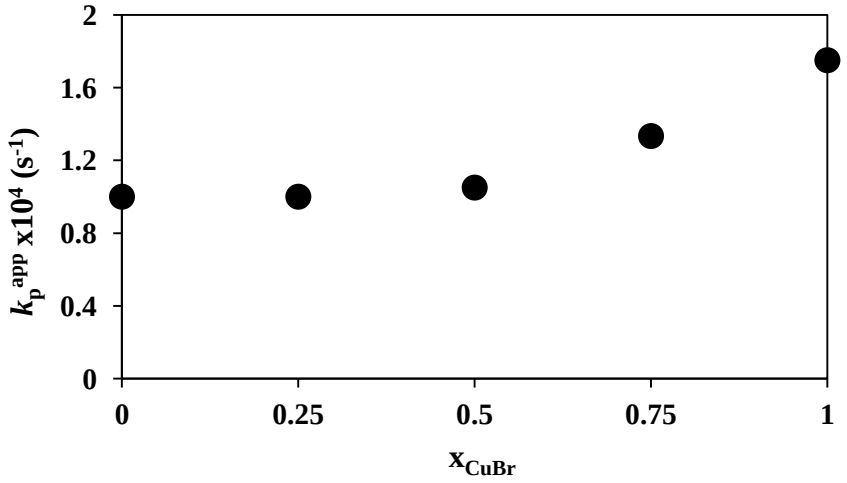


Figure 4.9 : Effect of CuBr fraction in the constant total catalyst amount ([CuBr+$CuBr_2$]) on k_p^{app} of AGET ATRP of St in 10% (v/v) toluene. [$CuBr_2$+CuBr]=$3.96x10^{-2}$mol/L, [St]:[EBrPr]:[CuBr+$CuBr_2$]:[PMDETA]= 200:1:1:1 at 110 ^oC.

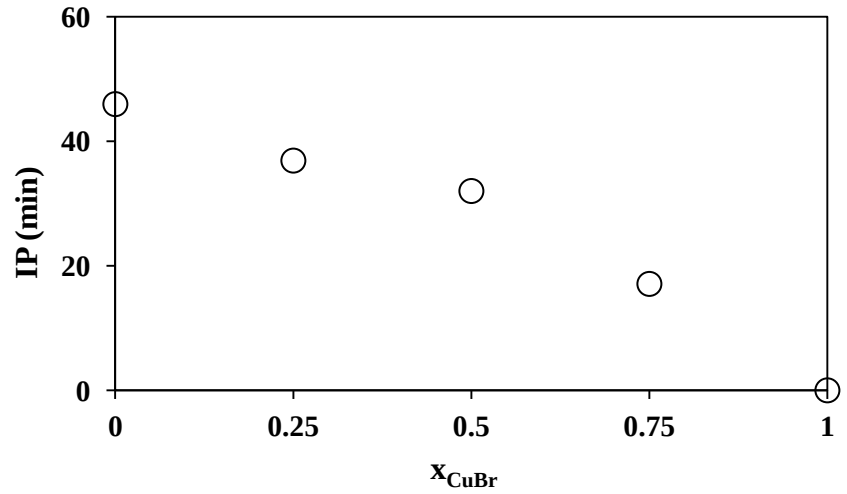


Figure 4.10 : Effect of CuBr fraction in the constant total catalyst amount ([$CuBr_2$+CuBr]) on IP of AGET ATRP of St in 10% (v/v) toluene. [$CuBr_2$+CuBr]=$3.96x10^{-2}$mol/L, [St]:[EBrPr]:[$CuBr_2$+CuBr]:[PMDETA]= 200:1:1:1 at 110 ^oC.

Additionally, the relationship between molecular weigt (M_n) and PDI versus monomer conversion with PMDETA as both ligand and reducing agent belonging to [St]:[EBrPr]:[$CuBr_2$]:[PMDETA]=200:1:1:1 in toluene is showed on Figure 4.11. M_n values of resultant polymers increased linearly with monomer conversion and relatively low polydispersity (PDI≈1.1) are observed like in DMF.

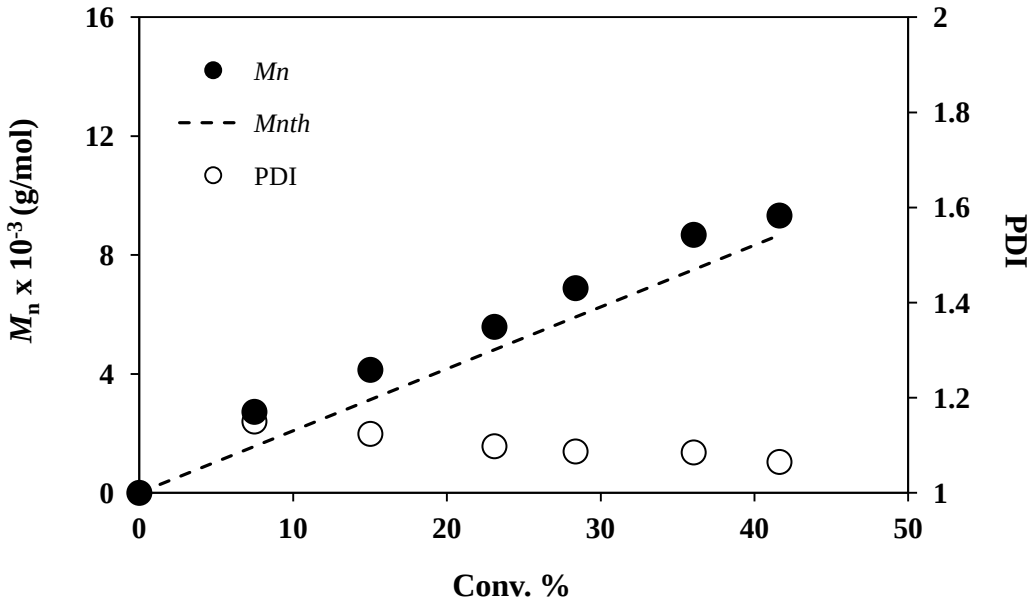


Figure 4.11 : Dependence of M_n and PDI on monomer conversion for AGET ATRP of St in 10 % (v/v) toluene. [St]= 7.91 mol/L, [St]:[EBrPr]:[$CuBr_2$]:[PMDETA]= 200:1:1:1 at 110 ^oC.

4.1.3 Comparison of AGET ATRP of styrene in DMF and toluene

The above results demonstrated that well-controlled polymerization of St via AGET ATRP in both less and high polar solvents. As seen on Figrure 4.12, unsuprisingly, polymerization was faster in homogenous than heterogenous, except the ligand/catalyt ratio at 0.75 and 1. The smaller amount of ligand as a reducing agent was also required to reach plato value in the heterogeneous than homogenous conditions. Since $CuBr_2$ was solubilized partially in toluene and solvated part conglomerated. Because of this aggregation, PMDETA could achieve to catalyst and reduced to $CuBr_2$ expediently. So the easy interaction between PMDETA and solute $CuBr_2$ in toluene made the IP shorter than in DMF (Figure 4.13).

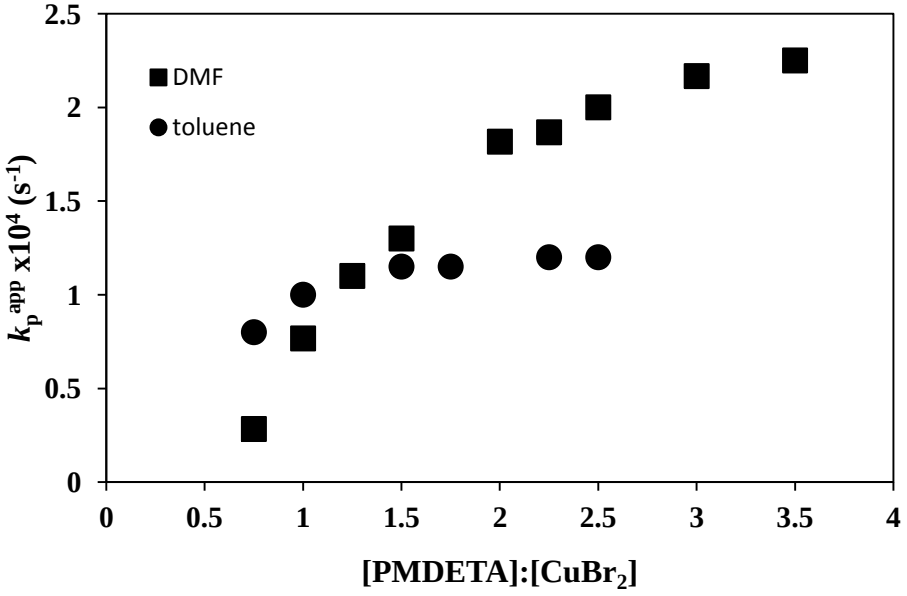


Figure 4.12 : Effect of PMDETA on k_p^{app} of AGET ATRP of St in 10% (v/v) DMF and toluene at 110 ^oC. [St]= 7.91 mol/L, [St]:[EBrPr]:[$CuBr_2$]= 200:1:1.

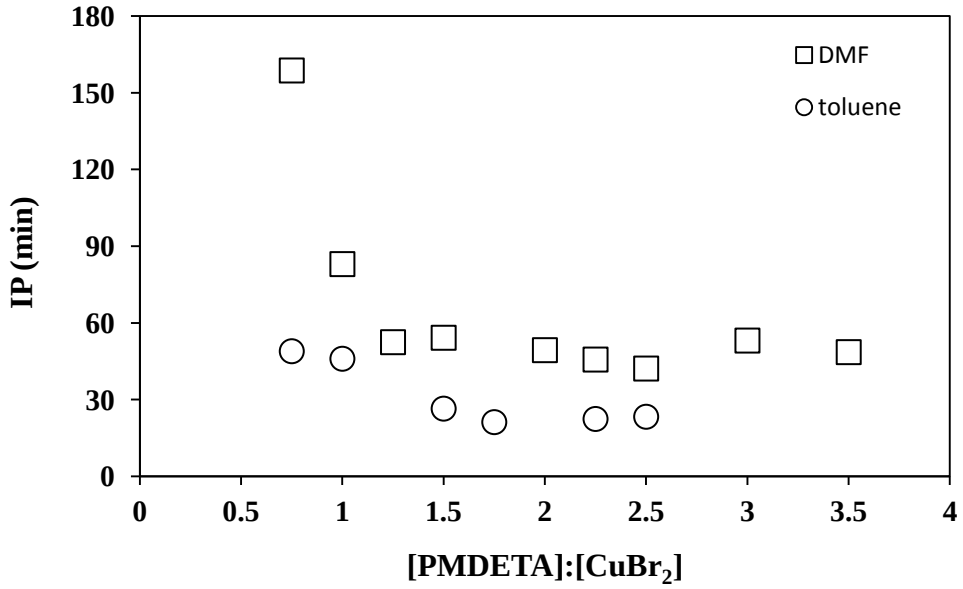


Figure 4.13 : Effect of PMDETA on IP of AGET ATRP of St in 10% (v/v) DMF and toluene at 110 ^oC. [St]= 7.91 mol/L, [St]:[EBrPr]:[$CuBr_2$]= 200:1:1.

When polymerizations using the $CuBr_2$-CuBr mixture as catalyst in DMF and tolene compared, as before mentioned The PMDETA/$CuBr_2$ ratio is 1, the polymerization in toluene was faster than DMF. However, in both conditions, the apparent rate constant (Figure 4.14), was rising with an increase in fraction of CuBr in the constant total amount of $CuBr_2$+CuBr also IP (Figure 4.15) was decreased with the increasing of CuBr in CuBr+$CuBr_2$ reached to "" when $CuBr_2$ in [CuBr+$CuBr_2$] is zero.

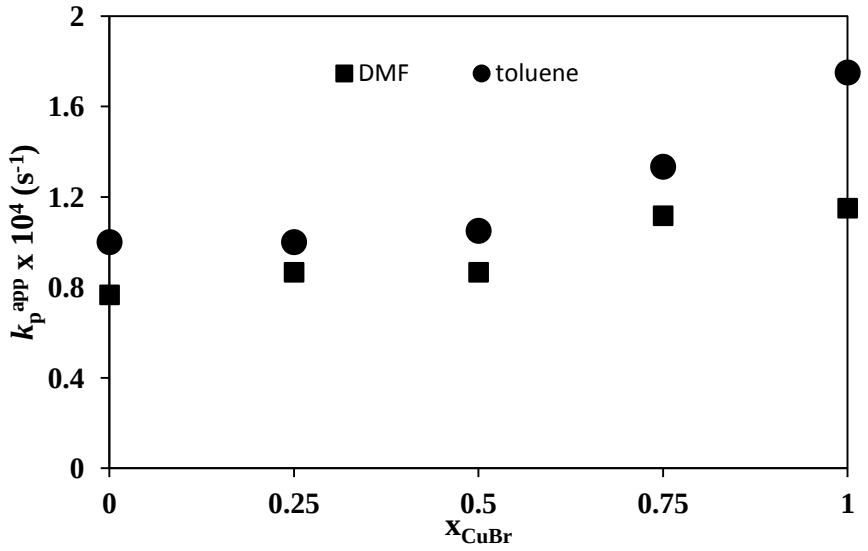


Figure 4.14 : Effect of CuBr fraction in the constant total catalyst amount ([CuBr+$CuBr_2$]) on k_p^{app} of AGET ATRP of St . [$CuBr_2$+CuBr]= $3.96x10^{-2}$ mol/L, [St]:[EBrPr]:[CuBr+$CuBr_2$]:[PMDETA]= 200:1:1:1 at 110 ^oC in 10% (v/v) DMF and toluene.

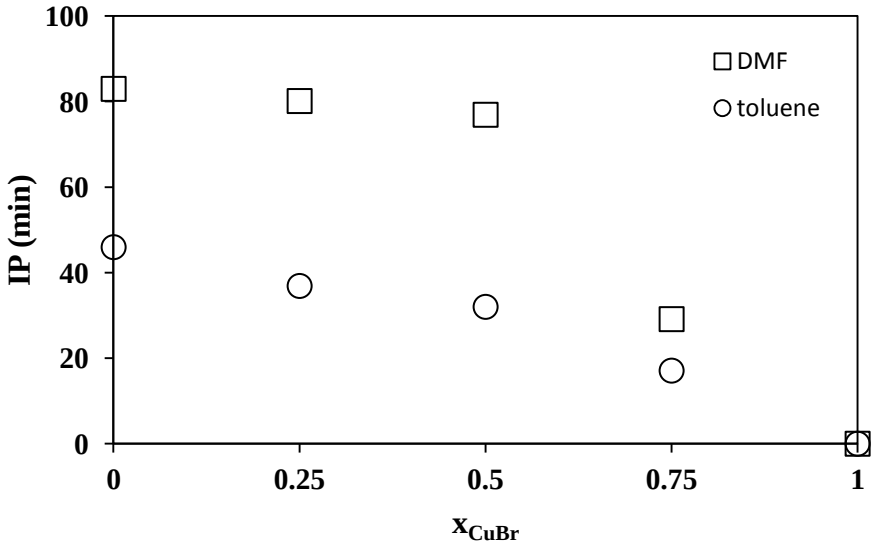


Figure 4.15 : Effect of CuBr fraction in the constant total catalyst amount ([$CuBr_2$+CuBr]) on IP of AGET ATRP of St. [$CuBr_2$+CuBr]= $3.96x10^{-2}$ mol/L, [St]:[EBrPr]:[$CuBr_2$+CuBr]:[PMDETA]= 200:1:1:1 at 110 ^oC in 10% (v/v) DMF and toulene.

Finally, the relationship between molecular weigt (M_n) versus monomer conversion with PMDETA as both ligand and reducing agent in DMF and toluene were scrutinized, it is clearly seen that M_n values of resultant polymers increased linearly with monomer conversion in both case. These results demonstrated that AGET ATRP of styrene with aliphatic nitrogen based ligands used as both reducing agents and ligands was well controlled. The difference between homogeneous, i.e, in DMF

and heterogeneous, i.e, in toluene conditions is the observed M_n is closer to theoretical values in heterogeneous (Figure 4.16).

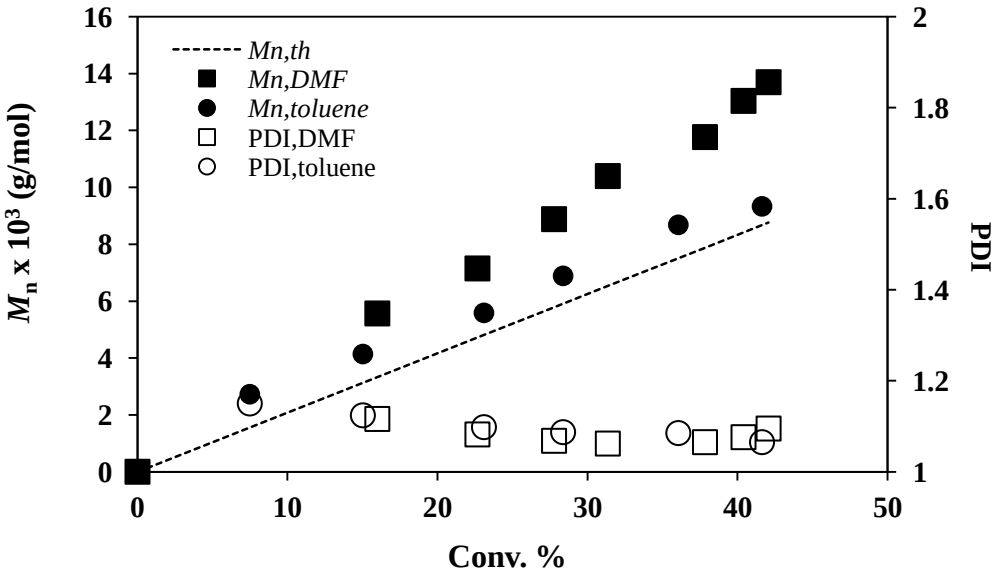


Figure 4.16 : Dependence of M_n on monomer conversion for AGET ATRP of St in 10% (v/v) DMF and toluene. [St]= 7.91 mol/L, [St]:[EBrPr]:[$CuBr_2$]:[PMDETA]= 200:1:1:1 at 110 ^oC.

4.1.4 Proposed mechanism possibilities for reduction of $CuBr_2$ by PMDETA

Weisset al. [59] prooved that triethylamine reduced $CuCl_2$ to CuCl and produced a cation radical species (Figure 4.17). Besides reduction of high-valent copper and manganese complexes to the low-valent metal salts by aliphatic amines through one electron transfer process was reported by Wang and Sayre [60] and Caudle and Pecoraro [61], respectively. After that, reduction of Cu(II) to Cu(I) salt by nitrogen-based ligands used for ATRP was reported by Kwak and Matyjaszewski based on mechanism proved by Weisset and coworkers. [14]. They demonstrated that linear bidendate ligand has the highest reducing potential followed by the linear tri and tetradentate ligand.

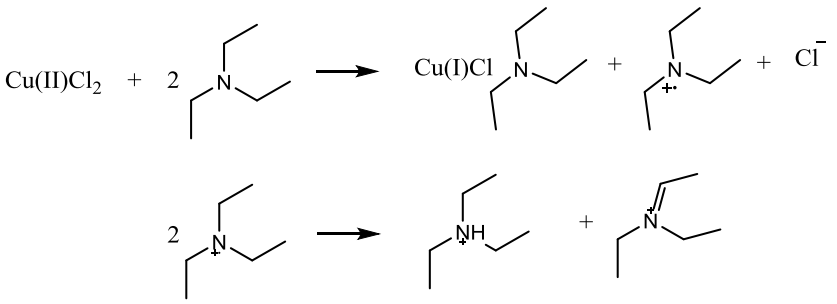


Figure 4.17 : Proposed mechanism of reduction $CuCl_2$ by triethylamine.

Due to PMDETA is tri dentate amine, there are various alternatives for generation of CuBr via electron transfer between nitrogen and $CuBr_2$. Based on above proposed mechanism, the reduction mechanisms of $CuBr_2$ by PMDETA are represented on Figure 4.18-a, b and c for one electron, two electrons and three electrons transfer, respectively. It is tought that ligand/metal ratio decides the number of electron, which transferred from ligand to metal in higher oxidation state (Figure 4.19). Only $3e^-$ transfers might be occurred when the ligand/metal ratio is 1.33 (Figure 4.18-c), 2 e^- could be transfered apart from 3 e^- in the ligand/metal ratio is 1.5, (Figure 4.18-b) and $1e^-$ along with 2 and 3 e^- transfer have to be occurred in the ligand/metal ratio is 2 (Figure 4.18-a) for reduction of total $CuBr_2$. The overall result of this study, with increasing PMDETA concentration, the polymerization rate accelerates and then reachs up plato value in both solvents. Because the difference of number in electron transfer affects the polymerization rate, the polymerization would be slower where the probility of the more electrons transfer were occurred. PMDETA/$CuBr_2$ ratio could be affected in number of electron transfer for reduction of $CuBr_2$, due to the solubility of metal salt and/or ligand-catalyst complex could be different in each solvent.

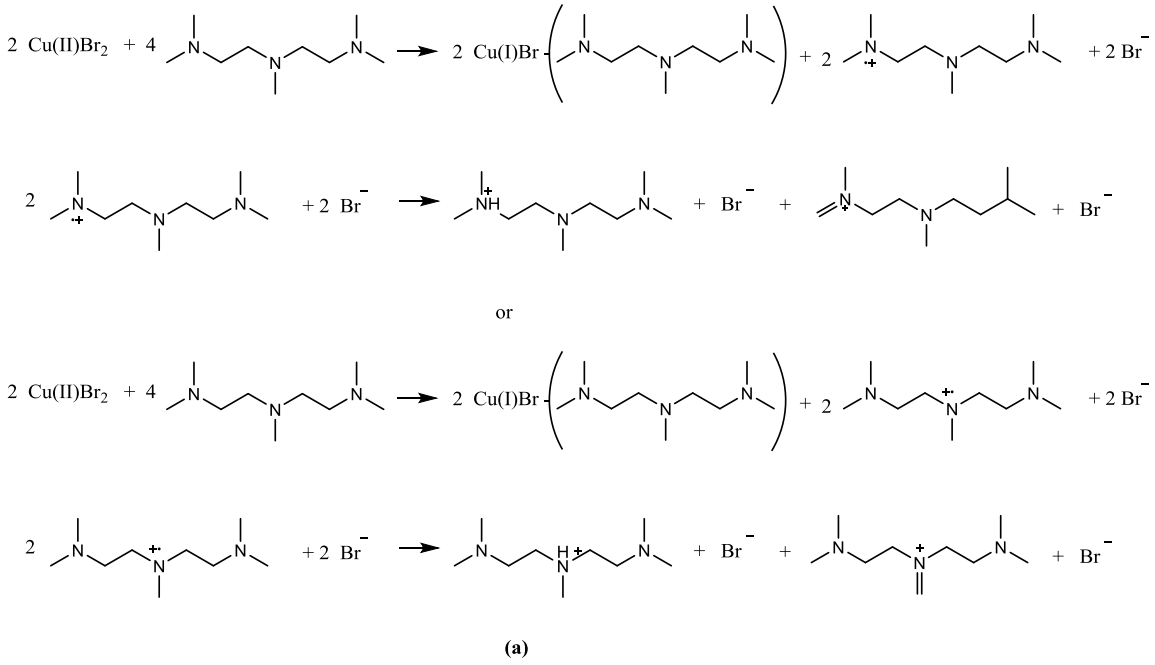


Figure 4.18 : Proposed mechanism of reduction $CuBr_2$ by PMDETA. a) 1 electron transfer b) 2 electrons transfer c) 3 electrons transfer

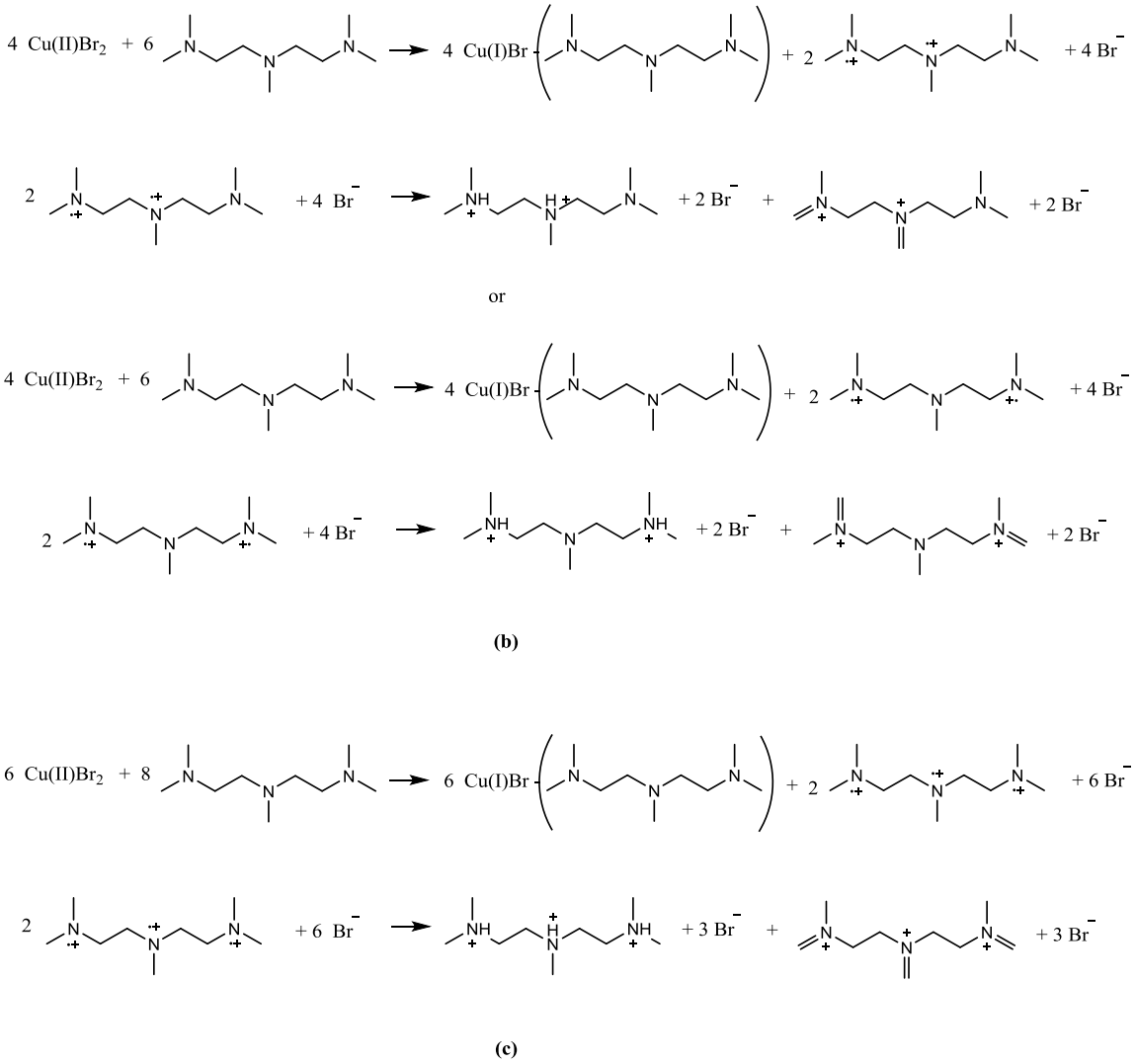


Figure 4.18 (cont): Proposed mechanism of reduction $CuBr_2$ by PMDETA. a) 1 electron transfer b) 2 electrons transfer c) 3 electrons transfer.

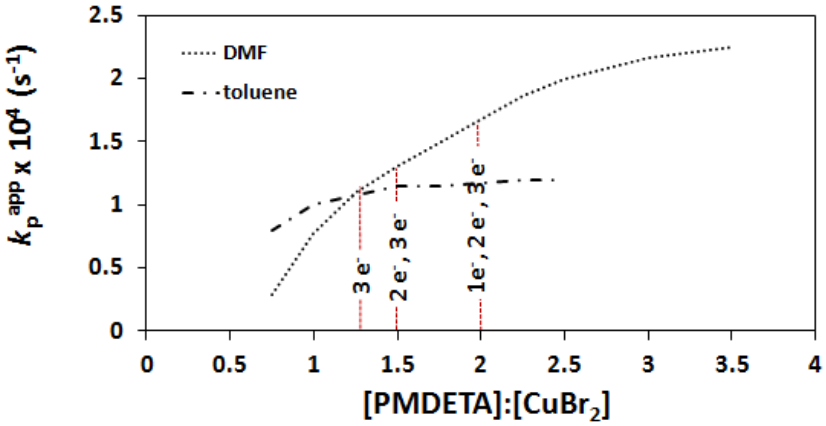


Figure 4.19 : Effect of ligand/catalyst ratio on k_p^{app} of AGET ATRP of St with probably e^- transfer numbers .

5. CONCLUSION

Using tri dentate linear amine as ligand and reducing agent in AGET ATRP process was focused on this study. For this aim, PMDETA is prefered as ligand, and AGET ATRP of styrene with copper-based catalyzed system was performed in both polar and non-polar solvents. To show effect of ligand on k_p^{app} and IP, various PMDETA concentrations were used while other components were in constant amount. The polymerization was accelerated by increasing of PMDETA concentration, the apparent rate constant reached up to plato value whereas with an increase in the content of PMDETA the induction period got shorter and reached certain value in both DMF and toluene because of non-equivalence of $CuBr_2$ and PMDETA. However, since $CuBr_2$ was solubilized partially in toluene, under heteregenous, i.e, toluene the amount of ligand for using reduction of $CuBr_2$ was smaller than homogeneous, i.e, DMF. Because of this, polymerization was faster, unlikewise IP was longer in homogenous than heterogenous conditions. In addition, $CuBr_2$/CuBr mixture was used as catalyst for the same conditions. Apparent rate constant was rising with an increase of CuBr fraction in the constant total catalyst amount [$CuBr_2$+CuBr]; on the other hand, IP was decreased with the increasing of fraction of CuBr in [CuBr+$CuBr_2$]. IP was reached to expected "zero" value when the $CuBr_2$ is none in [CuBr+$CuBr_2$] where AGET ATRP turn to normal ATRP in both conditions. GPC results showed that, M_n values of resultant polymers increased linearly with monomer conversion and relatively low polydispersity (PDI≈1.1) are observed in polar solvent like in non-polar solvent. These results demonstrated that because PMDETA contains reducer group in itself and makes up the deficiency of additional reducing agent, AGET ATRP of styrene was performed controlled well under heterogeneous and homogeneous conditions.

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PUBLICATIONS/PRESENTATIONS ON THE THESIS

- **BAYRAKTAR, M.,** ACAR, M. H.**,** AGET ATRP of Styrene Using PMDETA as Both Ligand and Reducing Agent, *3rd International Symposium on Controlled/Living Polymerization: From Synthesis to Applications*, May 1-4, 2014 Antalya, Turkey.